THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

SPATIAL CORRELATION AND MAGNETIC PROPERTIES OF TWO-ELECTRON SYSTEMS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

BY

RAYMOND WILLIAM MIRES

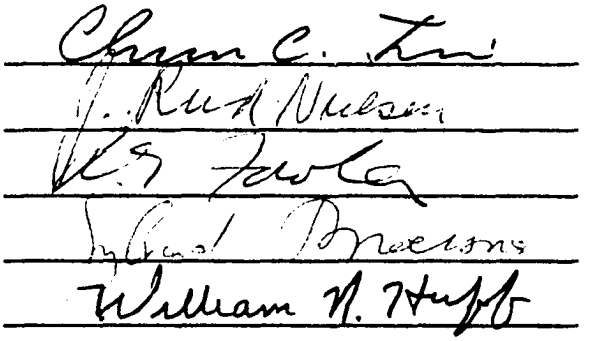
Norman, Oklahoma

1964

SPATIAL CORRELATION AND MAGNETIC PROPERTIES

OF TWO-ELECTRON SYSTEMS

APPROVED BY



DISSERTATION COMMITTEE

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Professor Chun C. Lin for suggesting the research problems considered in this work and for directing the work from its inception.

It is also a pleasure to acknowledge Dr. K. Hijikata for many enlightening discussions in the early stages of the correlation problem.

The author is also indebted to Texas Instruments, Inc. for supporting much of this work financially, and, in particular, to Dr. Turner Hasty for several helpful discussions and to Mr. Don Powell who assisted in much of the computer work. Mr. Powell also suggested a very helpful analytical expression.

Overdue appreciation is also extended to my wife, Beverly, and children, Sharilyn, Evin, and Leigh for their constant encouragement and sacrifice during the course of this work.

TABLE OF CONTENTS

LIST OF TABLES FOR PART I

LIST OF TABLES FOR PART II

LIST OF FIGURES FOR PART II

PART I. SPATIAL CORRELATION OF THE OUTER ELECTRONS IN TWO-ELECTRON SYSTEMS

CHAPTER I

INTRODUCTION

Several attempts have been made in recent years to obtain a more accurate solution of the two-electron Schrödinger equation by the use of correlated wave functions. The first such attempt was made by Hylleraas in his accurate treatment of the normal helium atom.[1] In this case the relative electronic coordinates were introduced into the wave function and the variation principle was used to determine some adjustable parameters. This method has been very successful and is considerably simpler than configuration interaction. Lennard-Jones and Pople (8) and Brickstock and Pople (2) have treated electron correlation in two-electron systems in a more general way for both the ground states and excited states. This is presented in Chapter II and it will be shown how the Hylleraas correlation becomes a special case. A general theory of correlated wave functions has also been published more

[1] For a bibliography of several of the early papers on electron correlation in the helium atom see Reference (10) in Bibliography.

recently by Szasz (14), however its complexity makes it impractical for the present work. Indeed, the object of this work is to develop a simplified method of including correlation.

Most of the previous work has dealt with the correlation between two s-electrons or between two electrons which do not have zero angular momentum but which are coupled together in their lowest multiplet level. The most recent work in the case of the latter was by Breene (1) in which the ^3P level of two and four p-electrons was treated with considerable improvement in the energy of that level. The main feature of this work is to use correlation of the two outer electrons in a simplified manner for obtaining more accurate theoretical values for the spacing between the various L-multiplets. In Chapter III the method will be applied to carbon-like atoms which have the ground configuration $(1s)^2(2s)^2(2p)^2$ and to atoms which have the ground configuration $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^2$. Here it will be assumed that the two outer electrons move in the spherically symmetric field of the nucleus and those electrons in the inner closed shells. The first-order wave function will be taken as a Clebsch-Gordan combination of hydrogenic orbitals with an effective charge determined by Slater's rules for $(2p)^2$ and by several other methods for the $(3d)^2$ case.

It is quite well established that the solutions of the Hartree-Fock (HF) equations provide, perhaps, the best

radial functions yet obtainable for a many-electron atom. In the analytic HF method one uses some intuition to decide on the most probable functional form of the radial functions and then uses the variation method to fix the adjustable parameters. Such a procedure has been used by R. E. Watson (15) to obtain radial functions for many possible configurations in the iron-series elements. Although Watson's is probably the best calculation yet made on these elements, an examination of his results reveals values of the Slater-Condon parameters $F^{(2)}(n\ell,n\ell)$ which are about 20% larger than the experimental values. Since, according to the Slater-Condon theory, the multiplet spacing depends quite strongly on these parameters one might expect Watson's results to give a poor fit of the experimentally determined multiplet spacing. This is indeed the case.

There are several ways to improve on Watson's results. First, the effect of configuration interaction could be superposed on the HF theory. This amounts to using a linear combination of Slater determinants instead of a single one and should certainly lower the energy, the higher levels being lowered more than the ones below them. This effect is obviously in the right direction to produce the necessary correction to Watson's results. Second, one might expect that although the HF equations provide for some correlation between electrons of like spin, they may not adequately include any correlation arising from opposite spins or from electrostatic

repulsion. Therefore, a Hylleraas-type of correlation could be superposed on the HF equations. This is roughly analogous to taking into account the effect of one or two additional configurations. It is this latter method which is considered in Chapter IV. A Hylleraas r_{12}-type of correlation is also used in this case and the theory is applied to the $(3d)^2$-type of transition metal ions for which the HF radial functions are available.

A discussion of the results for the HF model is given in Chapter V. Also presented here are some general remarks about the theory as well as some concluding statements.

CHAPTER II

SPATIAL CORRELATION IN TWO-ELECTRON SYSTEMS

Inclusion of Correlation

Spatial correlation of electrons has been treated in a somewhat general way in a series of papers by Lennard-Jones, Brickstock, and Pople (8),(2). These authors treated two-electron atoms and were successful in deriving a set of coupled differential equations for the radial part of the wave function. The theory was applied to the case of separable radial functions and to linear combinations of such. Some of the general formulation of these authors will be presented here and it will be shown that the Hylleraas r_{12}-type of function, which will be used later, results from a special choice of non-separable radial function.

The Hamiltonian of a system of two electrons moving in a spherically symmetric field V(r) may conveniently be written as[1]

$$H_{12} = H_1 + H_2 + H_{cor} \qquad (2.1)$$

where[2]

---

[1]Subscripts 1 and 2 will always refer to the outer electrons.

[2]Hartree atomic units will be used throughout this work unless otherwise stated.

$$H_1 = -\tfrac{1}{2}\nabla_1^2 + V(r_1),\quad H_2 = -\tfrac{1}{2}\nabla_2^2 + V(r_2),\quad H_{cor} = \frac{1}{r_{12}} - V(r_1,r_2) \tag{2.2}$$

In (2.2), r_{12} is the scalar distance between the two electrons, ∇^2 is the usual Laplace operator, and $V(r_1,r_2)$ is a function which represents the amount by which one electron screens the other from the central field of the core. The functional form of $V(r_1,r_2)$ is dictated by the choice of the central field $V(r)$. However, in most cases $V(r_1,r_2)$ will be an additive function of the form $f_1(r_1) + f_2(r_2)$ and for equivalent electrons f_1 and f_2 are the same function. For the latter case,

$$V(r_1,r_2) = 2Y(r_1). \tag{2.3}$$

The dependence on the choice of central field has still not been removed but merely shifted to the function $Y(r_1)$. If $V(r_1)$ is taken to be a central field which does not depend on the wave functions of the other electrons in the atom then the choice of the functional form of $Y(r_1)$ is almost arbitrary. This will be considered in the next chapter. For this case, however, one must make the additional assumptions that (2.1) and (2.2) are valid only if the Coulomb energy between the outer electron and the core electrons is included in $V(r_1)$ and if the exchange energy between the outer electron and the core is neglected. If these assumptions are made it is possible to write the total wave function as a product of the form $\Psi(\text{core})\cdot\Psi(1,2)$. This would cause an increase in the

total energy and one may expect, then, that spatial correlation could be used to pull the energy back down to its proper level. When used in this way, the spatial correlation should be regarded merely as an artifice for correcting the results obtained by using a poor approximation. Nevertheless, this hypothesis seems to be worth pursuing further because of its simplicity. A slightly more physical argument for spatial correlation is given in a later chapter.

Before leaving the discussion of the central field it should be pointed out that if $V(r_1)$ is the HF field for electron 1 then $Y(r_1)$ is a very complicated but known function depending on the orbital associated with electron 2. Also, (2.1) and (2.2) are perfectly valid without any additional assumptions.

The correlated two-electron wave function may be written as

$$\Psi_{LM}(1,2) = \psi^{o}(\vec{r}_1,\vec{r}_2) + \sum_k \psi_k(\vec{r}_1,\vec{r}_2)\, P_k(\cos\omega) \qquad (2.4)$$

where ω is the angle between the two radius vectors and $P_k(\cos\omega)$ is the ordinary Legendre polynomial. By letting ψ^{o} and ψ_k be functions of the vector distances it is possible to include states which are not spherically symmetric as well as those which are. $\psi^{o}(\vec{r}_1,\vec{r}_2)$ will be called the first-order wave function and will always be chosen as an exact eigenfunction of $H_1 + H_2$. The form of both ψ^{o} and ψ_k will be taken as .

$$\psi^{o}(\vec{r}_1,\vec{r}_2) = R^{o}_{n\ell}(r_1)\, R^{o}_{n\ell}(r_2)\, f_{LM}(\theta_1\varphi_1,\theta_2\varphi_2)$$

$$\psi_k(\vec{r}_1,\vec{r}_2) = R_k(r_1,r_2)\, f_{LM}(\theta_1\varphi_1,\theta_2\varphi_2) \qquad (2.5)$$

where f_{LM} is the appropriate Clebsch-Gordan combination of the two angular momenta which simultaneously diagonalizes the square of the total angular momentum operator L^2 and the operator L_z. This function gives the proper anti-symmetry property when multiplied by the spin functions for the two-electron system as demanded by the Pauli principle.

Although it will not be considered here, it is interesting to note at this point that a set of coupled differential equations whose solutions are $R_k(r_1,r_2)$ may be derived. The procedure is to substitute (2.5) into (2.4) and write down the two-electron Schrödinger equation using the operator (2.1). After re-coupling all the spherical harmonics and integrating over all the angles the result is the desired set of radial equations. Of course, some form of $Y(r)$ and $R^{o}_{n\ell}(r)$ must be assumed. The details of a similar procedure are presented in Reference (2).

In this work, the one-electron radial function $R^{o}_{n\ell}(r)$ will be treated as a known analytic form containing possibly some adjustable parameters. It is also convenient to assume an analytic form for $R_k(r_1,r_2)$. To make a reasonable choice of such function it is observed that H_{cor} in (2.1) contains $\frac{1}{r_{12}}$ which may be expanded as

$$\frac{1}{r_{12}} = \sum_k U_k(r_<, r_>)\ P_k(\cos\ \omega) \qquad (2.6)$$

where

$$U_k(r_<, r_>) \equiv \frac{r_<^k}{r_>^{k+1}} \qquad (2.7)$$

Here, $r_<$ is the lesser of r_1 and r_2, $r_>$ the greater of r_1 and r_2. Now r_{12} may also be expanded as

$$r_{12} = \sum_k V_k(r_<, r_>)\ P_k(\cos\ \omega) \qquad (2.8)$$

where

$$V_k(r_<, r_>) \equiv \frac{r_<^{k+2}}{(2k+3)\ r_>^{k+1}} - \frac{r_<^k}{(2k-1)\ r_>^{k-1}} \qquad (2.9)$$

Obviously the angular dependence in (2.6) and (2.8) is the same and any matrix element of r_{12} will have the same angular coefficients as those of $\frac{1}{r_{12}}$. Since (2.1) contains (2.6) it seems reasonable that the wave function $\Psi_{LM}(1,2)$ should also contain the relative electron coordinates in some manner. A somewhat heuristic clue is given by (2.8) and, indeed, it turns out to be convenient if one chooses $R_k(r_1, r_2)$ to have the following form

$$R_k(r_1, r_2) = R^o_{n\ell}(r_1)\ R^o_{n\ell}(r_2)\ c_k\ V_k(r_1, r_2) \qquad (2.10)$$

where c_k is a coefficient to be determined by the variation method. With this choice for the radial function and with (2.5), $\Psi_{LM}(1,2)$ may be written as

$$\Psi_{LM}(1,2) = \psi^{o}(\vec{r}_1,\vec{r}_2)\left[1 + \sum_{k} c_k\, V_k(r_1,r_2)\, P_k(\cos\omega)\right] \qquad (2.11)$$

It is interesting to note that if $c_k = 0$ for all k, $\Psi_{LM}(1,2)$ is approximated by the first-order function. This would give the familiar Slater-Condon parameters for each multiplet level. Also if c_k were the same constant for all k, $\Psi_{LM}(1,2)$ would become the conventional Hylleraas r_{12}-type of function given by

$$\Psi_{LM}(1,2) = \psi^{o}(\vec{r}_1,\vec{r}_2)(1 + c\, r_{12}) \qquad (2.12)$$

Either of these possibilities may be used with any suitable choice for the central field. It is the form (2.12) which will be investigated in this work. It should be pointed out that the correlation function as written in (2.12) does not lift the M-degeneracy in $\Psi_{LM}(1,2)$ nor does it destroy the orthogonality of $\Psi_{LM}(1,2)$ with respect to the various L-multiplets. It does, however, destroy the normalization and any calculation using $\Psi_{LM}(1,2)$ must be re-normalized.

Effective Hamiltonian and the Variation Method

Physically, the correlation should properly be associated with the wave function as in (2.12) since it is $\Psi_{LM}(1,2)$ which is supposed to represent the motion of the two electrons in the central field. However, for energy calculations it is more convenient to associate the correlation with the Hamiltonian. To do this, recall that the energy is given

by

$$(\Psi_{LM}|H_{12}|\Psi_{LM}) = (\psi^{o}(1 + c\, r_{12})|H_{12}|\psi^{o}(1 + c\, r_{12}))$$

which can be written as

$$(\Psi_{LM}|H_{12}|\Psi_{LM}) = (\psi^{o}|(1 + c\, r_{12})\, H_{12}(1 + c\, r_{12})|\psi^{o})$$

After expanding the operator in the last expression an effective Hamiltonian may be defined as

$$\overline{H}_{12} = H_{12} + c(r_{12}H_{12} + H_{12}r_{12}) + c^{2}r_{12}H_{12}r_{12} \qquad (2.13)$$

The energy may now be expressed as the diagonal element of this effective Hamiltonian in the original coupled representation. For equivalent electrons, (2.13) may be further expanded using (2.1), (2.2), (2.3) and noting that r_{12} commutes with those operators which are merely scalar functions of the radial distance. Furthermore, if ψ^{o} is chosen to be an eigenfunction of $H_1 + H_2$ then the matrix of this operator is diagonal and r_{12} commutes with it also. With these observations (2.13) becomes

$$\overline{H}_{12} = 2H_1 + \frac{1}{r_{12}} - 2Y(r_1) + 2c\left[2r_{12}H_1 + 1 - 2r_{12}Y(r_1)\right]$$
$$+ c^{2}\left[2r_{12}H_1r_{12} + r_{12} - 2r_{12}^{2}\,Y(r_1)\right] \qquad (2.14)$$

In (2.14), the term quadratic in c may be simplified by using a vector identity for the Laplacian operator. It is easy to derive the following operator identity

$$r_{12}H_1r_{12} = r_{12}^2H_1 - 1 - r_{12}\vec{\nabla}_1 r_{12}\cdot\vec{\nabla}_1 \qquad (2.15)$$

The last operator on the right in (2.15) appears very complicated but if the indicated operations are carried out, then in the diagonal element, integration over the angular coordinates of electron 2 causes all the terms to vanish except the first one, which in the operator is $r_1 d_{r_1}$ where d_{r_1} is the partial derivative operator with respect to r_1. This is true only for equivalent electrons and is a result of the selection rules on the spherical harmonics. Thus, in the diagonal element, one must evaluate a purely radial integral and it is easy to show that for any well-behaved radial function its value is always -3/2. This is worked out in Appendix I and will be used at the outset in (2.15). Also if one expands r_{12}^2 by the law of cosines the same selection rules cause the angular dependent term to vanish leaving only $\langle r_1^2 + r_2^2 \rangle = 2\langle r_1^2 \rangle$ for equivalent electrons. One is not allowed to make this last replacement, however, if r_{12}^2 is multiplied by one of the scalar functions of r_1, e.g., $r_{12}^2\, Y(r_1)$. With all of this, (2.15) may be written, for both electrons, as

$$2r_{12}H_1r_{12} = 4r_1^2H_1 + 1 \qquad (2.16)$$

Thus with the use of (2.16) the effective Hamiltonian now becomes

$$\bar{H}_{12} = 2H + \frac{1}{r_{12}} - 2Y(r_1) + 2c\left[2r_{12}H_1 + 1 - 2r_{12}Y(r_1)\right] + c^2\left[4r_1^2H_1 + 1 + r_{12} - 2r_1^2Y(r_1) - 2r_2^2Y(r_1)\right] \qquad (2.17)$$

The energy is now the diagonal element of (2.17) subject to the normalization condition

$$N \equiv (\Psi_{LM}(1,2)|\Psi_{LM}(1,2)) = 1 + 2c\ \langle r_{12}\rangle + 2c^2\ \langle r_1^2\rangle \qquad (2.18)$$

where the bra-ket notation has been used to denote a diagonal element in the $\ell_1\ \ell_2$ LM representation. The variational energy W is identified as

$$W = \langle \overline{H}_{12}\rangle / N \qquad (2.19)$$

The condition which determines the correlation coefficient c is given by the variational method as

$$d_c W = 0 \qquad (2.20)$$

where again d_c is the partial derivative operator with respect to c. Thus, in principle, the problem of using a correlated wave function is solved and it remains to see how effective such a procedure will be in theoretically predicting the multiplet spacing. This is done in the next two chapters for the $(2p)^2$ and $(3d)^2$ configurations.

CHAPTER III

THE HYDROGENIC CORE MODEL

Formulation for $(n, n-1)^2$ Configuration

In this section, the theory will be applied to two equivalent (n, n-1)-electrons moving in a purely hydrogenic type of central field. This implies that the one-electron radial functions should be of hydrogenic type and that the screening function Y(r) should be of the form

$$Y(r) = \frac{s}{r} \tag{3.1}$$

where s is a constant since only then will the central field be hydrogenic in form. Also V(r) will be chosen as

$$V(r) = \frac{Z'}{r} \tag{3.2}$$

where Z' is identified as the effective charge which makes the one-electron orbital an eigenfunction of the one-electron Hamiltonian given in (2.2). The choice of Z' will also determine s. All the properties of hydrogenic functions will be used, e.g.,

$$\text{one-electron energy} = -\frac{Z'^2}{2n^2}$$

$$\text{average value of } \frac{1}{r} = \frac{Z'}{n^2}, \text{ etc.}$$

With these remarks the diagonal element of (2.17) becomes

$$\langle \overline{H}_{12} \rangle = - (Z'^2/n^2) + Z' \sum_k a^{(k)} F^{(k)}(n\ell,n\ell) - (2Z's/n^2)$$

$$- 2c \left[(Z'/n^2) \sum_k a^{(k)} M^{(k)}(n\ell,n\ell) - 1 \right.$$

$$\left. + 2s \sum_k a^{(k)} N^{(k)}(n\ell,n\ell) \right] - c^2 \left[(s/Z')(2n+1)^2 \right.$$

$$\left. + n(2n+3) - (1/Z') \sum_k a^{(k)} M^{(k)}(n\ell,n\ell) \right] \qquad (3.3)$$

In (3.3) the radial integrals are defined as

$$F^{(k)}(n\ell,n\ell) = \iint U_k(r_<,r_>) |R^o_{n\ell}(r_1)|^2 |R^o_{n\ell}(r_2)|^2 r_1^2 r_2^2 dr_1 dr_2$$

$$M^{(k)}(n\ell,n\ell) = \iint V_k(r_<,r_>) |R^o_{n\ell}(r_1)|^2 |R^o_{n\ell}(r_2)|^2 r_1^2 r_2^2 dr_1 dr_2$$

$$N^{(k)}(n\ell,n\ell) = \iint \frac{1}{r_1} V_k(r_<,r_>) |R^o_{n\ell}(r_1)|^2 |R^o_{n\ell}(r_2)|^2 r_1^2 r_2^2 dr_1 dr_2 \qquad (3.4)$$

The Z'-dependence has already been extracted from the integrals in (3.4), i.e., to evaluate them the Z' in the radial functions should be set to unity. The $a^{(k)}$ coefficients in (3.3) are the angular coefficients which precede each of the Slater-Condon parameters for a given multiplet and are given by

$$a^{(k)} = \sum_{m_1 m_1'} C^{L\ell\ell}_{m_1 M-m_1} C^{L\ell\ell}_{m_1' M-m_1'} c^k(\ell m_1, \ell m_1') c^k(\ell M-m_1', \ell M-m_1) \qquad (3.5)$$

where $C^{L\ell\ell}_{m_1 M-m_1}$ are the well-known Clebsch-Gordan coefficients for two equivalent electrons and $c^k(\ell m, \ell m')$ are the result of integrating over the products of three spherical harmonics. Both of these coefficients are tabulated in any standard text on quantum mechanics (4).

The normalization condition (2.18) becomes

$$N = 1 + (2c/Z') \sum_k a^{(k)} M^{(k)}(n\ell, n\ell) + c^2(2n + 1)(n + 1) \frac{n^2}{Z'^2} . \tag{3.6}$$

To facilitate the discussion of particular configurations it is convenient to define two other quantities. Obviously, if the correlation coefficient c were set to zero the energy of the various levels would be that obtained from the usual Slater-Condon theory of multiplets. This energy will be denoted as E. The energy obtained by using the correlated wave functions is given by (2.19) and identified as W and should be lower than E. Since the positive difference between these two quantities is not a true correlation energy it will be referred to simply as the energy correction and denoted by

$$E_c = E - W \tag{3.7}$$

while the experimental value for the multiplet energy is E_{exp}.

The $(2p)^2$ Configuration

In the carbon-like atoms it is assumed that the two outer electrons move in the central field of the nucleus and

the spherically symmetric field produced by the closed electronic shells $(1s)^2(2s)^2$. However, due to the statistical nature of the quantum theory, one of the outer electrons is supposed to spend a fraction of its time between the other 2p-electron and the core, thus producing some screening also. According to Slater's rules for determining effective nuclear charge this fraction should be 0.35 for anything but 1s-electrons (11). Thus, s is taken as this fraction and Z' is given by the same set of rules as

$$Z' = Z_{core} - s = Z - 2.4 - s$$

where Z is the true atomic number.

According to the Slater-Condon theory the energy of the multiplets arising from $(2p)^2$ is given by

$$E(^1S) = F^{(o)} + (10/25)\ F^{(2)}$$

$$E(^1D) = F^{(o)} + (1/25)\ F^{(2)}$$

$$E(^3P) = F^{(o)} - (5/25)\ F^{(2)}$$

and

$$\frac{E(^1S) - E(^1D)}{E(^1D) - E(^3P)} = 1.5 \qquad (3.8)$$

This ratio is obviously independent of the radial function and thus independent of the choice of the central field. Furthermore, it should be the same for all carbon-like atoms. This ratio has been measured experimentally for the three

elements studied here and found to be somewhat less than 1.5 (7). The experimental values are:

C I	1.13
N II	1.14
O III	1.14

The ratio (3.8) may be adopted as a criterion for measuring the improvement obtained by using the correlated wave function.

In Table I are presented some results of using the present method for the three atoms listed above. The main features of these results are the following: the higher energy levels are suppressed more as would be expected from configuration interaction and the ratio (3.8) is considerably less than the experimental values but improves with increasing ionization. The latter feature is also displayed in Table II where the individual multiplet separations were calculated and compared with the observed values. From this table it is obvious that the $^1D - {}^3P$ separation is in quite good agreement with the observed value and the error remains rather constant as the stage of ionization is increased. This is probably because both of these levels lie low enough so that the $\frac{1}{r_{12}}$ perturbation always remains quite small compared to the central field potential thus making the core model a reasonably good approximation. In the $^1S - {}^1D$ separation practically all of the error must be attributed

TABLE I. RESULTS FOR $(2p)^2$. ALL ENERGIES IN a.u.

Atom	Multiplet	c	E	W	E_c	Ratio
C I	^1S	0.670	-2.504785	-2.609547	0.104762	0.75
	^1D	0.308	-2.697622	-2.640127	0.032505	
	^3P	0.078	-2.676171	-2.680801	0.004629	
N II	^1S	0.582	-4.337988	-4.451176	0.113188	0.93
	^1D	0.244	-4.472461	-4.506738	0.034277	
	^3P	0.076	-4.562109	-4.566786	0.004677	
C III	^1S	0.534	-6.671191	-6.789910	0.118718	1.03
	^1D	0.234	-6.837305	-6.872462	0.035157	
	^3P	0.075	-6.948046	-6.952753	0.004706	

TABLE II. MULTIPLET SEPARATIONS FOR $(2p)^2$ IN a.u.

		Calculated			
Atom	Separation	No Corr.	With Corr.	Observed[a]	% Error
C I	$^1S - {}^1D$	0.102837	0.030580	0.052190	41.4
	$^1D - {}^3P$	0.068549	0.040674	0.046315	12.2
N II	$^1S - {}^1D$	0.134473	0.055562	0.079155	29.8
	$^1D - {}^3P$	0.089648	0.060048	0.069380	13.4
O III	$^1S - {}^1D$	0.166114	0.082552	0.104400	20.9
	$^1D - {}^3P$	0.110741	0.080291	0.091415	12.2

[a]Observed values taken from Slater, Ref. (11).

to the ^1S level alone. This level lies so high that the $\frac{1}{r_{12}}$ energy is not small compared to the central field potential thus making the set of hydrogenic orbitals a poor basis set for the unperturbed Hamiltonian. The improvement in this separation with stage of ionization is explained by essentially the same argument, i.e., as the nuclear charge increases the interaction with the central field increases. This decreases the relative magnitude of the $\frac{1}{r_{12}}$ term which causes the core model to become more accurate.

In all of the results the absolute significance of the deviations from the observed values must be attributed to the choice of the correlation function $(1 + c\ r_{12})$. Indeed, there are other ways to include the relative electronic coordinates and it is difficult to ascertain the best method. The particular function used here was chosen because of its simplicity but on the basis of the results it is felt that it represents a fairly good choice for the ^1D and ^3P levels.

The $(3d)^2$ Configuration

The procedure here is the same as in the $(2p)^2$ case except for the choice of the central field, i.e., the choice of Z' and s. Now the two outer electrons move in the field of the nucleus and the spherically symmetric central field of the closed electronic shells $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6$. According to Slater's rules for effective charge, s should again be 0.35 and Z' should be given by (see Ref. 11)

$$Z' = 0.65Z - 11.35 + 0.35p \qquad (3.9)$$

where p is the stage of ionization, equal to zero for the neutral atom, unity for a singly charged ion, etc. The calculation has been carried out using these rules for the isoelectronic sequence Ti III - Ni IX and a few of the significant results are presented in Table III. It is obvious from the table that the calculated values for the multiplet spacings are in poor agreement with the observed values and the improvement with increasing ionization is only slight. This is not too surprising since it is well known that Slater's rules become a poor approximation very rapidly as one proceeds to the larger atoms. There is much evidence that these rules produce a value of Z' which is much too small and the inclusion of correlation cannot do anything but make matters worse since its effect is to suppress the energy levels differentially as is indicated by the correlation coefficient. The competition between improvement with increasing ionization and the decreasing validity of Slater's rules as one goes to higher Z is responsible for the slight improvement with stage of ionization.

The above problem was not apparent in the $(2p)^2$ case because the effective charge determined by this method is always within the range of, or slightly higher than, the values obtained from a simplified Hartree-Fock calculation (11).

From Table III the stability of the correlation coefficient for the ^3F level as one proceeds through the

TABLE III. CALCULATED AND OBSERVED MULTIPLET SPACINGS USING SLATER'S EFFECTIVE CHARGE[a]

Atom, Z'	Level	c	Separation	Calculated cm^{-1}	Observed cm^{-1}
Ti III	^1S	1.62			
3.65	^1G	0.463	$^1G - {}^3F$	2630	14398
	^3P	0.386	$^3P - {}^3F$	2341	10570
	^1D	0.303	$^1D - {}^3F$	2040	8473
	^3F	0.117			
V IV	^1S	1.12	$^1S - {}^3F$	6381	---
4.65	^1G	0.391	$^1G - {}^3F$	4580	18389
	^3P	0.321	$^3P - {}^3F$	3985	13180
	^1D	0.271	$^1D - {}^3F$	3363	10960
	^3F	0.110			
Cr V	^1S	0.929	$^1S - {}^3F$	10380	---
5.65	^1G	0.354	$^1G - {}^3F$	6716	[22060]
	^3P	0.288	$^3P - {}^3F$	5733	15500
	^1D	0.253	$^1D - {}^3F$	4792	13200
	^3F	0.105			
Mn VI	^1S	0.825	$^1S - {}^3F$	14857	---
6.65	^1G	0.331	$^1G - {}^3F$	8967	25511
	^3P	0.269	$^3P - {}^3F$	7536	17782
	^1D	0.241	$^1D - {}^3F$	6282	15336
	^3F	0.109			
Fe VII	^1S	0.759	$^1S - {}^3F$	19711	---
7.65	^1G	0.315	$^1G - {}^3F$	11303	28915
	^3P	0.256	$^3P - {}^3F$	9386	20037
	^1D	0.233	$^1D - {}^3F$	7825	17475
	^3F	0.099			
Co VIII	^1S	0.714	$^1S - {}^3F$	24842	---
8.65	^1G	0.304	$^1G - {}^3F$	13691	---
	^3P	0.246	$^3P - {}^3F$	11256	---
	^1D	0.227	$^1D - {}^3F$	9393	---
	^3F	0.098			
Ni IX	^1S	0.680	$^1S - {}^3F$	30190	---
9.65	^1G	0.296	$^1G - {}^3F$	16118	---
	^3P	0.239	$^3P - {}^3F$	13142	---
	^1D	0.223	$^1D - {}^3F$	10983	---
	^3F	0.097			

[a]All observed values taken from "Atomic Energy Levels", Circular 467, U.S. Dept. of Commerce, National Bureau of Standards, 1952.

isoelectronic sequence is very striking but no conclusions can be made from it due to the obviously poor choice for the zero-order functions.

Better methods exist for determining effective charge. The method of ionization potentials has been used by Lane and Lin to determine Z' for many configurations in the iron-series elements (7). For each atom in the sequence their results for Z' were considerably larger than those given by (3.9) and they give results for the multiplet spacings without correlation which are only slightly less than the observed values. However, because of the differential suppression of the levels with the inclusion of correlation this small deviation is sufficient to produce the same general trends as given in Table III. The basic differences between the results of Table III and the results of a calculation using these larger values of Z' were a more rapid improvement with ionization and the correlation coefficients in each case were approximately one-half as large as those in the table. The calculation was carried out using s = 0.35 and s = 0.5 which is the value determined by these two writers and appears to be slightly more realistic than the former value due to Slater.

From the above discussion it seems at least heuristically obvious that if one uses some other criterion for choosing Z' and if this choice produces multiplet results which are too large then the inclusion of correlation should

produce a correction in the right direction. One possibility is to choose Z' which will reproduce the experimentally determined value of $F^{(2)}(3d,3d)$. The difficulty here is deciding on the correct experimental value to use since several experimenters have some quite different results. Cady has measured $F^{(2)}(3d,3d)$ and $F^{(4)}(3d,3d)$ for probably the largest number of the transition elements having a $(3d)^2$ electron configuration (3). His results for $F^{(2)}(3d,3d)$ appear in Table IV as well as the Z' (exp Z') calculated from them using the relation

$$F^{(2)}(3d,3d) = 202.499\ Z'\ cm^{-1} \qquad (3.10)$$

Also in Table IV are values of Z' (HF Z') calculated by (3.10) using Watson's Hartree-Fock results (15).

The results of the correlation calculation using Exp Z' and s = 0.5 are given in Table V for those atoms in Table IV for which the multiplets have been observed experimentally. The correlation coefficient is tabulated for the same order of levels as in Table III. The improvement with ionization is rather rapid here but the inclusion of correlation appears to over-correct the Slater-Condon theory for this choice of central field.

To retain the theoretical nature of this work the HF Z' from Table IV were used in a similar calculation. This was done for two values of s, 0.35 and 0.5, for each atom. These results are presented in Table VI where the correlation coefficient for each multiplet level is given in the same

TABLE IV. EXPERIMENTAL $F^{(2)}(3d,3d)$ DATA IN CM^{-1} AND EFFECTIVE CHARGE

	Ti III	V IV	Cr V	Mn VI	Fe VII	Co VIII	Ni IX
$F^{(2)}(3d,3d)$	1110	1456	1758	2062	2402	2670	2871
Exp Z'	5.40	7.19	8.68	10.18	11.86	13.18	14.18
HF Z'	6.77	8.26	9.52	---	---	---	---

TABLE V. EFFECT OF CORRELATION USING EXP Z'

Atom	c	Separation	Without Correlation (cm^{-1})	With Correlation (cm^{-1})	Observed Spacings (cm^{-1})
Ti III	0.798	$^1S - {}^3F$	35436	12453	14053?
	0.279	$^1G - {}^3F$	14186	7805	14398
	0.219	$^3P - {}^3F$	10664	6603	10570
	0.191	$^1D - {}^3F$	9210	5565	8473
	0.059				
V IV	0.656	$^1S - {}^3F$	46490	20571	---
	0.253	$^1G - {}^3F$	18613	11822	18389
	0.197	$^3P - {}^3F$	13992	9770	13180
	0.179	$^1D - {}^3F$	12084	8225	10960
	0.058				
Cr V	0.609	$^1S - {}^3F$	56125	28420	
	0.252	$^1G - {}^3F$	22470	15444	[22060]
	0.189	$^3P - {}^3F$	16891	12581	15500
	0.175	$^1D - {}^3F$	14588	10605	13200
	0.057				
Mn VI	0.578	$^1S - {}^3F$	65824	36739	---
	0.237	$^1G - {}^3F$	26353	19147	25511
	0.184	$^3P - {}^3F$	19810	15437	17782
	0.172	$^1D - {}^3F$	17109	13034	15336
	0.056				
Fe VII	0.554	$^1S - {}^3F$	76686	46384	---
	0.231	$^1G - {}^3F$	30703	23349	28915
	0.179	$^3P - {}^3F$	23079	18655	20037
	0.170	$^1D - {}^3F$	19932	15780	17475
	0.056				

TABLE VI. EFFECT OF CORRELATION USING HF Z'. (ALL ENERGIES IN CM^{-1}).

Atom	Separation	Observed Spacing	s = 0.35			s = 0.5		
			c	Without Correlation	With Correlation	c	Without Correlation	With Correlation
Ti III	$^1S - {}^3F$	14053?	0.815	43775	17644	0.674	43775	18458
	$^1G - {}^3F$	14398	0.329	17526	9247	0.256	17526	11047
	$^3P - {}^3F$	10570	0.267	13174	7761	0.200	13174	8985
	$^1D - {}^3F$	8473	0.240	11378	6470	0.181	11378	7563
			0.120			0.058		
V IV	$^1S - {}^3F$	---	0.729	53409	22812	0.620	53409	26159
	$^1G - {}^3F$	18389	0.308	21383	12754	0.246	21383	14412
	$^3P - {}^3F$	13180	0.249	16074	10525	0.191	16074	11786
	$^1D - {}^3F$	10960	0.230	13882	8779	0.176	13882	9930
			0.099			0.057		
Cr V	$^1S - {}^3F$	---	0.688	61556	29485	0.591	61556	33043
	$^1G - {}^3F$	[22060]	0.297	24645	15801	0.239	24645	17509
	$^3P - {}^3F$	15500	0.240	18526	12897	0.186	18526	14178
	$^1D - {}^3F$	13200	0.223	16000	10776	0.173	16000	11962
			0.097			0.057		

order as in the previous tables. Again the correction seems to be over-emphasized with the results using correlation being about as far below the observed values as they are above without correlation. The difference between the s = 0.35 and s = 0.5 cases seems to be insignificant for predicting the multiplet structure. However, for all choices of Z' the results turned out to be slightly better for the larger value of s. This gives some support to the work of Lane and Lin. An obvious result of Table VI is that the values of c are considerably smaller for s = 0.5 than for s = 0.35. This is because c depends quite strongly on the "uncorrelated energy" E and the larger value of s produces a larger absolute magnitude for E as one would expect if the screening is increased. No further conclusion can be made from this observation, however, since each choice of central field produces new values for c.

In the next chapter the more realistic Hartree-Fock atom will be considered in which Z' and s are no longer arbitrary. Thus one could expect some improvement in the results.

CHAPTER IV

THE HARTREE-FOCK ATOM

The results of the last chapter made it obvious that the over-simplified hydrogenic core model was not adequate for predicting the multiplet structure of the ions of the first transition elements. The indication was that the multiplet spacing was sensitive to the uncorrelated energy of the L - multiplets for which the hydrogenic core model is a poor approximation. Thus, it seems natural to extend the correlation effect to the more accurate Hartree-Fock field.

Hartree-Fock Theory of Two-Electron Systems

Only a brief outline of the Hartree-Fock theory for two 3d-electrons will be given here. Consider an atom having Z protons and N electrons, two of these N electrons being in a single incomplete group which lies outside of a number of complete groups, or closed shells. These closed shells will be referred to as the core. Let the two outer electrons be denoted by 1,2 and the core electrons by the indices i,j where each of the latter runs from 3 to N (over the core electrons only). The Hamiltonian for the entire atom can be written as

$$H_a = \sum_{i=1}^{N} H_i + \sum_{i,j=1}^{N}{}' \frac{1}{r_{ij}} \qquad (4.1)$$

where H_i is the one-electron Hamiltonian given by

$$H_i = -\frac{1}{2}\nabla_i^2 - (Z/r_i) \qquad (4.2)$$

Equation (4.1) may also be written as

$$H_a = \sum_{i=3}^{N} H_i + \sum_{i,j=3}^{N}{}' \frac{1}{r_{ij}} + \sum_{j=3}^{N} \frac{1}{r_{1j}} + \sum_{j=3}^{N} \frac{1}{r_{2j}} + H_1 + H_2 + \frac{1}{r_{12}} \qquad (4.3)$$

The terms in (4.3) may be identified as follows:

$H_c \equiv \sum_{i=3}^{N} H_i + \sum_{i,j=3}^{N}{}' \frac{1}{r_{ij}}$: contains coordinates of the core electrons only

$H_{c-e} \equiv \sum_{j=3}^{N} \frac{1}{r_{1j}} + \sum_{j=3}^{N} \frac{1}{r_{2j}}$: contains coordinates of all the electrons

$H_{12} \equiv H_1 + H_2 + \frac{1}{r_{12}}$: contains coordinates of the outer electrons only

With this notation then

$$H_a = H_c + H_{c-e} + H_{12} \qquad (4.4)$$

If H_{c-e} were not present in (4.4) one could expect to separate the complete wave function into a product as $\Psi_a = \phi(c)\,\phi(1,2)$ and the energy would be given by $E_a = E_c + E_{12}$. However, this is not the case and, furthermore, Ψ_a must be anti-symmetric with respect to interchange in the

coordinates of any two electrons including those electrons in the core with either of the two outer electrons. A single Slater-type determinantal wave function constructed from one-electron orbitals $\varphi_{n\ell}(i)$ is sufficient to satisfy the anti-symmetry property. When this is used with (4.3) the total energy may be written as

$$E_a = E_c + \sum_{j=3}^{N} J_{1j} + \sum_{j=3}^{N} J_{2j} - \sum_{j=3}^{N} K_{1j} - \sum_{j=3}^{N} K_{2j} + E_1 + E_2 + J_{12} \tag{4.5}$$

The Coulomb and exchange integrals are defined as

$$J_{1j} = \iint \varphi^*_{3d}(1)\, \varphi^*_{n\ell}(j)\, \frac{1}{r_{1j}}\, \varphi_{3d}(1)\, \varphi_{n\ell}(j)\, d\tau_1\, d\tau_j$$

$$K_{1j} = \iint \varphi^*_{3d}(1)\, \varphi^*_{n\ell}(j)\, \frac{1}{r_{1j}}\, \varphi_{n\ell}(1)\, \varphi_{3d}(j)\, d\tau_1\, d\tau_j \tag{4.6}$$

$$J_{12} = \iint \varphi^*_{3d}(1)\, \varphi^*_{3d}(2)\, \frac{1}{r_{12}}\, \varphi_{3d}(1)\, \varphi_{3d}(2)\, d\tau_1\, d\tau_2$$

The complete HF equation for the 3d-orbital is obtained by varying this orbital, subject to the usual normalization and orthogonality conditions, in such a way that E_a in (4.5) is a minimum. The angular integrals may be integrated at the outset and the minimization process produces a differential equation for the radial part of the 3d-orbital. The result, as given by Slater (12), is

$$\left\{ -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} - \frac{1}{r_1}\left[\sum_{\substack{\text{all core} \\ \text{electrons}}} N_j(n\ell)\, Y_o(n\ell, 3d; r_1) \right. \right. \tag{4.7}$$

$$+ \frac{1}{2\sqrt{5}} \sum_{\substack{\text{all core} \\ \text{electrons}}} \frac{N_j(n\ell)}{(2\ell_j+1)^{\frac{1}{2}}} \sum_k c^k(2,0;\ \ell_j,0)\ Y_k(n\ell,3d;r_1)$$

$$\times \frac{R_{n\ell}(r_1)}{R_{3d}(r_1)} \Big] + \frac{1}{r_1} \sum_k a^{(k)}\ Y_k(3d,3d;\ r_1) \Big\}\ R_{3d}(r_1) = -\ \epsilon_1\ R_{3d}(r_1)$$

In (4.7), $N_j(n\ell)$ is the number of electrons in the $n\ell$-closed shell, $c^k(2,0;\ell_j,0)$ are the coefficients discussed in connection with (3.5), $a^{(k)}$ are the same as given by (3.5) with one exception to be discussed later, and the $Y_k(n\ell,3d;\ r_1)$ are functions obtained by integrating the Coulomb integral over one of the electrons only. These functions were first introduced by Hartree and later generalized by Slater (11). They are defined as

$$Y_k(n\ell,3d;r_1) = \frac{1}{r_1^k} \int_0^{r_1} R_{n\ell}(r_2)\ R_{3d}(r_2) r_2^{k+2}\ dr_2 + r_1^{k+1} \int_{r_1}^{\infty} R_{n\ell}(r_2)\ R_{3d}(r_2) r_2^{-k+1}\ dr_2 \tag{4.8}$$

Also in (4.7), ϵ_1 according to Koopman's theorem is the ionization energy of the first 3d-electron.

It is obvious that the unknown radial function will be different for each multiplet level because the $a^{(k)}$ coefficients will change. This is referred to as the unrestricted HF method. In the restricted HF method, one finds the center of gravity, or average of the configuration (a of c) as it

is called, of all the terms and minimizes this energy with respect to the radial function. The result is a similar one-electron differential equation whose solution is a single radial function which best fits all the multiplet levels. Precisely the same equation is obtained by substituting $a^{(k)}_{\text{a of c}}$ for $a^{(k)}$ in (4.7) where these coefficients are related as follows.

$$a^{(k)}_{\text{a of c}} = \frac{\sum_{L,S} (2L+1)(2S+1)\, a^{(k)}}{\sum_{L,S} (2L+1)(2S+1)} \tag{4.9}$$

For $(3d)^2$,

$$a^{(0)}_{\text{a of c}} = 1,\quad a^{(2)}_{\text{a of c}} = a^{(4)}_{\text{a of c}} = -\frac{2}{63} \tag{4.10}$$

There are two ways to obtain an approximate solution to (4.7). One is to use numerical integration, the other is an analytic method in which one uses some intuition to decide on a reasonable analytic form for $R_{3d}(r_1)$. This analytic form which contains some adjustable parameters is substituted into (4.7) and the parameters are adjusted to give a minimum value for ϵ_1. Such a procedure has been used by Watson, in most cases for the a of c (6). The form of Watson's 3d-function, which is the only one needed here, is

$$R_{3d}(r) = r^2(C_{12}e^{-s_{12}r} + C_{13}e^{-s_{13}r} + C_{14}e^{-s_{14}r} + C_{15}e^{-s_{15}r}) \tag{4.11}$$

where C_i and s_i are the adjustable parameters which are tabulated in Ref. (6) for the various ions of the iron-series elements. These results are probably the best yet obtained for these atoms and the ionization potentials are in good agreement with the observed values. However, the results for $F^{(2)}(3d,3d)$ and $F^{(4)}(3d,3d)$ are about 20% too large which causes the levels to be spaced too far apart as shown in Table VI. It is hoped that the inclusion of correlation will correct this situation.

Before leaving the HF theory it is worthwhile to interpret the various terms in (4.7). The first two terms represent the kinetic plus nuclear potential energy. The square bracket represents the shielding of the nucleus by the core electrons and the last term is the shielding produced by one of the 3d-electrons on the other. Both of the shielding terms are obviously functions of r_1 and are not constant as was assumed in the last chapter. From (4.7) the one-electron HF Hamiltonian can be written symbolically in an obvious notation as

$$H_1 = -\frac{1}{2}\nabla_1^2 - \frac{Z - s_c'(r_1) - s_2(r_1)}{r_1} \qquad (4.12)$$

To understand the assumptions underlying the hydrogenic core model of the last chapter it is only necessary to consider the form of $Y_o(n\ell,3d;r_1)$ and $Y_k(n\ell,3d;r_1)$ and, thus, the form of $s_c'(r_1)$. These functions always have the form

$$Y_o \sim 1 - e^{-cr_1}. \quad \text{(polynomial in } r_1\text{)}$$

$$Y_k \sim e^{-cr_1}. \quad \text{(polynomial in } r_1\text{)}$$

The constant term in Y_o when summed over all the electrons in the core gives N-2. Factoring this constant and denoting everything that remains between the square bracket in (4.7) simply by $-s_c(r_1)$, H_1 can be written as

$$H_1 = -\frac{1}{2}\nabla_1^2 - \frac{Z - N + 2 + s_c(r_1) - s_2(r_1)}{r_1}$$

or

$$H_1 = -\frac{1}{2}\nabla_1^2 - \frac{Z - N + 2}{r_1} - \frac{s_c(r_1)}{r_1} + \frac{s_2(r_1)}{r_1} \qquad (4.13)$$

Obviously, Z - N + 2 is the charge experienced by one of the outer electrons if it moved in the field of a hard spherical core. s_c and s_2 represent the statistical nature of the charge distribution. As written here s_c and s_2 are both positive quantities with s_c being a measure of the amount of time the core charge cloud spends outside the 3d-orbit causing an increase in effective charge and s_2 a measure of the amount of time the other 3d-electron spends between the core and the electron being considered and thus causes a decrease in effective charge. By Slater's rules these two quantities are taken as constants.

If (4.13) is used for the one-electron Hamiltonian, then for the whole atom,

$$H_a = H_c + H_1 + H_2 + (1/r_{12}) - Y(r_1) - Y(r_2) \qquad (4.14)$$

where $Y(r_1)$ has been written for $\frac{s_2(r_1)}{r_1}$ to bring the notation closer to that defined in Chapter I. Again for equivalent electrons this becomes

$$H_a = H_c + H_1 + H_2 + (1/r_{12}) - 2Y(r_1) \qquad (4.15)$$

From (4.15) it appears that H_{c-e} has been eliminated from H_a and Ψ_a could be written again as a simple product $\phi(c)\cdot\phi(1,2)$ where each of these is anti-symmetric with respect to interchange of any two of their separate electrons. It is obvious now that such a product amounts to neglecting the exchange between the outer electrons and the core electrons thus increasing the energy. Actually, H_{c-e} is not eliminated but has been distributed between the two outer electrons since one needs the orbitals for the core charge distribution. It will be shown that this calculation is not necessary when correlation is introduced since it is already included in Watson's radial functions. However, an explicit form of $Y(r_1)$ is needed.

Effect of Correlation

Since the correlation function is related to the coordinates of the outer electrons only, H_c may be dropped from (4.15). This is because it will make no contribution to c when the variation method is used. The effective Hamiltonian (2.17) may now be used with H_1 given by (4.13)

or (4.7) and $Y(r_1)$ given as

$$Y(r_1) = \frac{1}{r_1} \sum_k a^{(k)} \, Y_k(3d,3d;r_1) \qquad (4.16)$$

The explicit form of $Y_k(3d,3d;r_1)$ is given in the Appendix.

If the unrestricted HF theory is used the $a^{(k)}$ coefficients in (4.16) and those arising from integration of $\frac{1}{r_{12}}$ in (4.15) will be identical resulting in some cancellation in the last two terms of (4.15). It is easy to show that in this case (4.15) can just as well be written, after dropping H_c, as

$$H_{12} = H_1 + H_2 - (1/r_{12}) \qquad (4.16)$$

where the HF functions are now eigenfunctions of the one-electron Hamiltonians. To retain the latter property in the a of c case one must use (4.15) as written with $a^{(k)}$ given by (4.9). Matrix elements containing $Y(r_1)$ then have to be evaluated.

The diagonal element of (2.17) becomes

$$\langle \bar{H}_{12} \rangle = - 2\epsilon_1 + \sum_k a^{(k)} \, F^{(k)}(3d,3d) - 2\langle Y(r_1) \rangle$$

$$- 2c \left[2\epsilon_1 \sum_k a^{(k)} \, M^{(k)}(3d,3d) - 1 \right.$$

$$\left. + 2 \sum_k a^{(k)} \, R^{(k)}(3d,3d) \right] - c^2 \left[4\epsilon_1 \langle r_1^2 \rangle - 1 \right.$$

$$- \sum_k a^{(k)} M^{(k)}(3d,3d) + 2\langle r_1^2 Y(r_1)\rangle + 2\langle r_1^2\rangle\langle Y(r_1)\rangle \tag{4.17}$$

where the radial integrals are defined in (3.4) except $R^{(k)}(3d,3d)$ is defined as

$$R^{(k)}(3d,3d) = \iint Y(r_1)\, V_k(r_<,r_>)\, |R_{3d}(r_1)|^2\, |R_{3d}(r_2)|^2 \times r_1^2 r_2^2 dr_1 dr_2 \tag{4.18}$$

and ϵ_1 is the one-electron ionization energy calculated by Watson and entered as a positive quantity in (4.17). The $a^{(k)}$ which appear explicitly in (4.17) are those appropriate to the multiplet level being considered and are given by (3.5). The normalization condition is the same as (2.18).

For studying the multiplet spacing it is convenient to eliminate the one-electron ionization energy from (4.17). This can be done by grouping the first terms in each line of (4.17) together and factoring the matrix element of $(1 + cr_{12})^2$ which is just the normalization constant. After normalizing, the result is

$$W' = -2\epsilon_1 + (1/N)\left\{ \sum_k a^{(k)} F^{(k)}(3d,3d) - 2\langle Y(r_1)\rangle \right. \tag{4.18}$$

$$+ 2c\left[1 - 2\sum_k a^{(k)} R^{(k)}(3d,3d)\right]$$

$$\left. + c^2\left[1 + \sum_k a^{(k)} M^{(k)}(3d,3d) - 2\langle r_1^2 Y(r_1)\rangle - 2\langle r_1^2\rangle\langle Y(r_1)\rangle\right]\right\}$$

where N is again given by (2.18). By introducing other radial integrals and making use of the definition of $Y(r_1)$, (4.18) can be written for the a of c case, after dropping $-2\varepsilon_1$, as

$$W = \frac{1}{N}\Big\{ \sum_k (a^{(k)} - 2a^{(k)}_{\text{a of c}})\, F^{(k)}(3d,3d)$$

$$+ 2c\Big[1 - 2\sum_{k,k'} a^{(k)}\, a^{(k')}_{\text{a of c}}\, R^{(k)}(3d,3d;k)\Big]$$

$$+ c^2\Big[1 + \sum_k a^{(k)}\, M^{(k)}(3d,3d) - 2\sum_k a^{(k)}_{\text{a of c}}\, N^{(k)}(3d,3d)$$

$$- 2R^{(2)}(3d)\sum_k a^{(k)}_{\text{a of c}}\, F^{(k)}(3d,3d)\Big]\Big\} \qquad (4.19)$$

and

$$N = 1 + 2c\sum_k a^{(k)}\, M^{(k)}(3d,3d) + 2c^2\, R^{(2)}(3d) \qquad (4.20)$$

where the new radial integrals are defined as

$$R^{(k)}(3d,3d;k') = \iint \frac{1}{r_1} V_k(r_<,r_>)\, Y_{k'}(3d,3d;r_1)\, |R_{3d}(r_1)R_{3d}(r_2)|^2 \times r_1^2 r_2^2 dr_1 dr_2$$

$$N^{(k)}(3d,3d) = \iint r_1\, Y_k(3d,3d;r_1)\, |R_{3d}(r_1)R_{3d}(r_2)|^2\, r_1^2 r_2^2 dr_1 dr_2$$

$$R^{(2)}(3d) = \int r_1^2 |R_{3d}(r_1)|^2\, r_1^2 dr_1$$

Written in this form, all $a^{(k)}$ coefficients are explicitly stated, those without the a of c subscript belong to the appropriate L-multiplet being considered. The radial integrals are to be calculated using a of c radial functions. If the unrestricted HF theory is used the $a^{(k)}_{a\ of\ c}$ need only be replaced by $a^{(k)}$ and the unrestricted radial functions used in the integrals.

The variational method (2.20) is now used to find the correlation coefficient and thus the multiplet energies. Such a calculation has been made for the two $(3d)^2$-type ions whose a of c radial functions were available, namely, Ti III and Cr V. These results are given in Table VII. The experimental data are the same as in the previous tables.

TABLE VII. (a) RESULTS FOR Ti III USING RESTRICTED HF THEORY

Level	c	E (a.u.)	W (a.u.)	E_c (cm^{-1})
^3F	0.070478	-0.677022	-0.681043	882
^1D	0.177952	-0.626789	-0.647514	7359
^3P	0.198211	-0.616256	-0.639331	5064
^1G	0.245053	-0.598432	-0.631686	7298
^1S	0.587385	-0.482976	-0.627349	31686

		Calculated (cm^{-1})		Deviation	
Spacing	Obs.(cm^{-1})	No Corr.	With Corr.	No. Corr.	With Corr.
$^1D - ^3F$	8473	11025	7359	+ 30.1%	- 13.1%
$^3P - ^3F$	10570	13337	9155	+ 26.2%	- 13.4%
$^1G - ^3F$	14398	17249	10833	+ 19.8%	- 24.8%
$^1S - ^3F$	14053(?)	42588	11784	---	---

TABLE VII. (b) RESULTS FOR Cr V USING RESTRICTED HF THEORY

Level	c	E (a.u.)	W (a.u.)	E_c (cm^{-1})
^3F	0.072525	-0.934298	-0.938856	1000
^1D	0.179709	-0.861935	-0.885135	5092
^3P	0.195103	-0.847776	-0.873253	5592
^1G	0.241684	-0.821558	-0.858753	8163
^1S	0.554401	-0.655069	-0.783719	28235

		Calculated (cm^{-1})		Deviation	
Spacing	Obs.(cm^{-1})	No Corr.	With Corr.	No Corr.	With Corr.
$^1D - ^3F$	13200	15882	11790	+ 20.3%	- 10.7%
$^3P - ^3F$	15500	18989	14398	+ 22.5%	- 7.1%
$^1G - ^3F$	[22060]	24744	17581	+ 12.2%	- 20.3%
$^1S - ^3F$	---	61284	34049	---	---

CHAPTER V

DISCUSSION OF RESULTS AND CONCLUDING REMARKS

There are several features contained in Table VII which are obvious at the outset. First, while the percentage deviation is improved, the inclusion of correlation still over-corrects the multiplet spacing. Second, the percentage deviation decreases with increasing atomic number. Third, the results are very nearly the same as those obtained from the hydrogenic core model using the HF value for Z' and 0.5 for the screening constant. These will be discussed in reverse order in the following paragraphs.

Considerable insight may be gained by asking how the minimum energy depends upon various quantities. To do this, write W in the form

$$W = \frac{a_1 + a_2 c + a_3 c^2}{1 + a_4 c + a_5 c^2} \equiv \frac{1}{N} (a_1 + a_2 c + a_3 c^2) \qquad (5.1)$$

where

$$a_1 = \langle 1/r_{12} \rangle - 2 \langle Y(r_1) \rangle$$

$$a_2 = 2[1 - 2\langle r_{12}\, Y(r_1) \rangle]$$

$$a_3 = 1 + \langle r_{12} \rangle - 2\langle r_1^2\, Y(r_1) \rangle - 2\langle r_1^2 \rangle \langle Y(r_1) \rangle$$

$$a_4 = 2\ \langle r_{12} \rangle$$

$$a_5 = 2\ \langle r_1^2 \rangle$$

Now assume W has already been minimized and the proper value of c inserted in (5.1). To find out how W depends on the individual matrix elements, vary W with respect to each, as well as with respect to c. One gets

$$\begin{aligned} N\ \delta W = {} & [-W(a_4 + 2a_5 c) + a_2 + 2a_3 c]\delta c + c(c - 2W)\ \delta\ \langle r_{12} \rangle \\ & - 2c^2 (W - \langle Y(r_1) \rangle)\ \delta \langle r_1^2 \rangle + \delta \langle 1/r_{12} \rangle \\ & - 2(1 + c^2\ \langle r_1^2 \rangle)\ \delta\ \langle Y(r_1) \rangle - 4c\ \delta\ \langle r_{12} Y(r_1) \rangle \\ & - 2c^2\ \delta\ \langle r_1^2 Y(r_1) \rangle \end{aligned} \tag{5.2}$$

Since c is a function of all the a's, δc is not independent of variations in them. The expression for c is obtained from the variational principle and is

$$c = \frac{-(a_3 - a_1 a_5) + \sqrt{(a_3 - a_1 a_5)^2 - (a_3 a_4 - a_2 a_5)(a_2 - a_1 a_4)}}{(a_3 a_4 - a_2 a_5)}$$

For calculations of δc the radical may be expanded without making much error in δc. Then

$$c \approx -\frac{1}{2} \frac{a_2 - a_1 a_4}{a_3 - a_1 a_5} \left[1 + \frac{1}{4} \frac{(a_3 a_4 - a_2 a_5)(a_2 - a_1 a_4)}{(a_3 - a_1 a_5)^2} \right] \tag{5.3}$$

Equation (5.3) may now be varied with respect to each of the

a's. The result is

$$\delta c = -\frac{1}{2(a_3 - a_1a_5)}\left\{\left[-a_4 + \frac{a_5(a_2 - a_1a_4)}{a_3 - a_1a_5}\right.\right.$$

$$+ \frac{a_4(a_3a_4 - a_2a_5)(a_2 - a_1a_4)}{2(a_3 - a_1a_5)^2}$$

$$\left.\left. - \frac{3a_5(a_2 - a_1a_4)^2(a_3a_4 - a_2a_5)}{4(a_3 - a_1a_5)^2}\right]\delta a_1 + \left[1\right.\right.$$

$$\left.\left. - \frac{(a_3a_4 - a_2a_5)(a_2 - a_1a_4)}{2(a_3 - a_1a_5)^2} - \frac{a_5(a_2 - a_1a_4)^2}{4(a_3 - a_1a_5)^2}\right]\delta a_2\right.$$

$$+ \left[- \frac{a_2 - a_1a_4}{a_3 - a_1a_5} - \frac{a_4(a_2 - a_1a_4)^2}{4(a_3 - a_1a_5)^2}\right.$$

$$\left. + \frac{3(a_3a_4 - a_2a_5)(a_2 - a_1a_4)^2}{4(a_3 - a_1a_5)^2}\right]\delta a_3 + \left[- a_1\right.$$

$$\left. + \frac{a_1(a_3a_4 - a_2a_5)(a_2 - a_1a_4)}{2(a_3 - a_1a_5)^2} - \frac{a_3(a_2 - a_1a_4)^2}{4(a_3 - a_1a_5)^2}\right]\delta a_4$$

$$+ \left[\frac{a_1(a_2 - a_1a_4)}{a_3 - a_1a_5} - \frac{a_2(a_2 - a_1a_4)^2}{4(a_3 - a_1a_5)^2}\right.$$

$$\left.\left. - \frac{3a_1(a_3a_4 - a_2a_5)(a_2 - a_1a_4)^2}{4(a_3 - a_1a_5)^3}\right]\delta a_5\right\}$$

In terms of the individual matrix elements the first term in (5.2) becomes, for the ^3F level of Ti III,

$$\text{first term in (5.2)} = -0.0623\delta\langle 1/r_{12}\rangle + 0.1144\delta\langle Y(r_1)\rangle - 0.0485\delta\langle r_{12}Y(r_1)\rangle + 0.0193\delta\langle r_{12}\rangle - 0.0041\delta\langle r_1^2 Y(r_1)\rangle + 0.0008\delta\langle r_1^2\rangle$$

The remaining terms in (5.2) for the same level give

$$\text{remaining terms} = 1.00\delta\langle 1/r_{12}\rangle - 2.05\delta\langle Y(r_1)\rangle - 0.280\delta\langle r_{12}Y(r_1)\rangle + 0.243\delta\langle r_{12}\rangle - 0.010\delta\langle r_1^2 Y(r_1)\rangle + 0.013\delta\langle r_1^2\rangle$$

It is obvious that, compared with the remaining terms, the first term is relatively insensitive to a variation in the individual matrix elements. Such variations could be generated by round-off error in the calculation but this is believed to be small since all matrix elements were calculated using 16-digit arithmetic and retaining only the first 8-digits. Therefore, these variations may be regarded as arising from the choice of the radial functions and the screening function $Y(r_1)$. After combining the last two expressions the result is

$$N\delta W = 0.938\delta\langle 1/r_{12}\rangle - 1.94\delta\langle Y(r_1)\rangle - 0.328\delta\langle r_{12}Y(r_1)\rangle$$

$$+ 0.2628\langle r_{12}\rangle - 0.0148\langle r_1^2 Y(r_1)\rangle + 0.0148\langle r_1^2\rangle$$

It is seen that the largest contribution arises from $\langle 1/r_{12}\rangle$ and $\langle Y(r_1)\rangle$ but these determine the uncorrelated energy and certainly the results should depend quite strongly on them as was stated earlier. The next largest contribution is from those matrix elements containing the screening function $Y(r_1)$. It was not apparent earlier that the minimum energy was so sensitive to this function. It is also interesting to note that $\langle Y(r_1)\rangle$ would not change the multiplet spacings without correlation since it is the same for all the terms (in the a of c approximation), but with correlation it makes a different contribution to each multiplet through the matrix element $\langle r_{12} Y(r_1)\rangle$.

It can now be understood how the hydrogenic model can give results so near those of the HF model. In the hydrogenic case $Y(r_1)$ was chosen almost arbitrarily and with such freedom of choice it is possible to make W depend on this function to about the same degree as in the more accurate case. This is apparently what happened in using the HF Z' and s = 0.5 for the hydrogenic calculation. This is justified since $\langle r_{12}\rangle$ and $\langle r_1^2\rangle$ depend only on Z' and HF Z' causes these matrix elements to be about the same as their HF values. This is shown below for ^3F of Ti III.

$$\langle r_{12}\rangle_{Hyd}/\langle r_{12}\rangle_{HF} = 1.08$$

$$\langle r_1^2\rangle_{Hyd}/\langle r_1^2\rangle_{HF} = 1.10$$

The improvement with atomic number, or with stage of ionization, is expected for the same reason as in the hydrogenic model. The central field becomes stronger, making the HF functions more accurate so that the correlation effect is smaller.

It is not obvious why inclusion of correlation should over-correct the multiplet spacing. However, the HF model does contain several basic assumptions, among them are the use of a single configuration or a single Slater determinant to describe the ion and short analytical expansions for the radial part of the one-electron orbitals. These two were inherent in Watson's original work and his results represent the most current attempt, and perhaps the only one, to solve the Hartree-Fock equations analytically for the first-row transition elements. Basically, the inclusion of correlation was suppose to correct for these two assumptions. Although Watson obtained, for some ions, the unrestricted radial functions these were always for the ground level only and since all five multiplet levels were to be considered here it was decided to use the a of c approximation so that the same radial function could be used for each of the levels. This approximation neglects the polarization of the closed-shell core by the outer electrons, an effect which is expected to contribute very little to the multiplet spacing. However, Watson and Freeman have shown recently that this effect makes an appreciable contribution to certain magnetic properties

of these ions, especially the Sternheimer anti-shielding factor (5), (6), (16).

The remaining assumptions are inherent in this work. The first of these is the assumption that the atomic wave function can be written as a product of the core wave function and a two-electron wave function for the outer electrons. This neglects the exchange between the outer electrons and the core. However, this was included by Watson in obtaining the HF functions and it would not affect the energy levels until the correlation function is introduced. In this work the antisymmetric two-electron function was simply multiplied by the symmetric correlation function, thus leaving the symmetry unchanged. As a consequence, the central field in which the outer electrons "move" is unaffected by the correlation function. This introduces an approximation since the central field is partially determined in the Hartree-Fock formulation by one of the outer-electron orbitals which is being correlated. To remove this approximation the two 3d-orbitals should be correlated first and the resulting function antisymmetrized again. This would properly correct the core potential but at the expense of introducing an enormous number of three-electron integrals into the calculation. Although Szasz has devised a method for evaluating such integrals (13), the increased difficulty defeats part of the objectives of this work. At first, it was believed that this alteration in the core would produce a small effect, perhaps

of the order of the spin polarization described by Watson and Freeman and referred to in the above paragraph. In fact, if correlated wave functions are to be used in a study of the magnetic properties the above approximation should not be used. It is difficult to even estimate its effect and could indeed account for a large part of the over-correction here.

One other consideration which belongs to this work is the choice of the correlation function. It was desired to use a function which introduces the relative electronic coordinate. There are many such functions which do this, for example, $1 + cr_{12}^2$, $1 + c(r_1 - r_2)^2$, and $1 + c \cos \omega$ where ω is the angle between radius vectors of the two electrons. The second of these introduces pure radial correlation very similar to the radial part of the first one. The calculation was carried through for the hydrogenic model using this function and it produced very little change in the energy levels. The last function introduces pure angular correlation. The problem was formulated for this function also but the calculation was not carried out since it was already known that $1 + cr_{12}$ produces much simpler matrix elements and there was no a priori reason for favoring $\cos \omega$ over r_{12}. Very similar problems arise with $1 + cr_{12}^2$ since the angular part of this function is also proportional to $\cos \omega$. Furthermore, $\cos \omega$ has no diagonal elements for any of the multiplet levels so it could never produce an effect

similar to configuration interaction as does $1 + cr_{12}$. These considerations made it seem reasonable to use the latter function.

In using $1 + cr_{12}$, the tacit assumption is being made that this is the only type of correlation that exists when, indeed, there may be other types co-existing with it. Judging from the size of the correlation coefficient the r_{12}-type becomes more prominent with increasing energy which implies that all the other types become less prominent. If this is the case the other types would suppress the ^3F level a little more thus decreasing the over-correction. This is purely conjecture but it seems to have some merit.

In conclusion, it is still felt that spatial correlation is an effective way of treating the many-electron atom. The major unsolved problem is still the choice of the correlation function and the proper way to include it while still retaining a degree of simplicity which appears to be several orders of magnitude greater than configuration interaction. It is worth pointing out again that $1 + cr_{12}$ is roughly equivalent to using two or three higher configurations but the symmetry problems are reduced considerably, mainly because r_{12} has the same angular dependence as $\frac{1}{r_{12}}$ and the symmetry considerations for this operator within a single configuration are well known.

PART II. MAGNETIC PROPERTIES OF V_2O_3

CHAPTER VI

INTRODUCTION

Recent theoretical and experimental work on V^{+++} in corundum has provided much information about the magnetic properties of the transition element ion and the crystalline properties of the Al_2O_3 structure (19). This work was based on the properties of single crystals having high magnetic dilution so that the nearest cation neighbors to the vanadium ion were aluminum which are known to be diamagnetic (33). Thus, Al_2O_3 acts merely as a host crystal, providing only an electrostatic field at the position of the magnetic ion. In pure V_2O_3 the situation is quite different. Although the crystal structure is still the corundum-type (24), at least in the paramagnetic region, the nearest cation neighbors are now vanadium and the ionic exchange interactions must be included. Some experimental work has been done on pure V_2O_3 (21), (20) which shows that the magnetic susceptibility undergoes two transitions of quite different character. The first of these occurs around 168°K and is a cooperative transition since the crystal symmetry is apparently lowered

to monoclinic as the temperature is decreased through 168°K (24). The electrical conductivity also indicates a metallic to semiconducting transition as the temperature is lowered through this point (29). Upon raising the temperature through this point the crystal was found to crumble into small pieces (36). The second transition occurs over a temperature range from about 390°K to about 500°K. According to Goodenough (24) this is a non-cooperative transition since it produces no change in the crystal symmetry. The susceptibility over this temperature range is constant. Moreover, the Curie-Weiss law is not obeyed over any temperature range. None of these characteristics is observed in the dilute crystal and it is inferred that if the exchange interaction were properly included they would account for this anamolous behavior. The present theory applies to temperatures above 170°K and the exchange interactions are included in a purely phenomenological manner with some parameters to be adjusted by fitting the theory to the experimental data. The theory does not predict either of the transitions and must be regarded as a correction to the Curie-Weiss law over the separate temperature ranges of 170°K to 370°K and 500°K to about 700°K.

The one-ion approximation is adopted here as in the case of the dilute crystal. The Hamiltonian is then the same with the addition of the exchange term. Furthermore, the ground configuration of V^{+++} is $(3d)^2$ and the usual approximation of a two-electron system moving in the field of a

shielded nucleus will be made. The Hamiltonian can then be written as

$$H = H_1 + H_2 + (e^2/r_{12}) + V_c + V_t + H_{s-o} + H_{ex} + \mu_o(\vec{L} + 2\vec{S})\cdot\vec{H} \ . \tag{6.1}$$

The various terms in (6.1) have the following meaning.

$H_i = -(\hbar^2/2m)\nabla_i^2 + U(r_i)$: one-electron Hamiltonian with central field potential $U(r_i)$.

(e^2/r_{12}): electrostatic energy operator between the two electrons.

V_c: potential energy for the cubic electrostatic field.

V_t: potential energy for the trigonal electrostatic field.

H_{s-o}: spin-orbit interaction energy.

H_{ex}: ionic exchange interaction energy.

$\mu_o(\vec{L} + 2\vec{S})\cdot\vec{H}$: interaction with external magnetic field where μ_o is the Bohr magneton.

It is well known that in a $(d)^2$ configuration the electrostatic energy operator produces the multiplet terms ^3F, ^1D, ^3P, ^1G, ^1S in order of increasing energy. Taking the first three terms in (6.1) as the unperturbed Hamiltonian H_o the eigenfunctions become the usual Clebsch-Gordan combination of one-electron orbitals. These are tabulated in Reference 32 for the ^3F and ^3P terms. This provides a starting point for a successive perturbation treatment of the remaining terms in the Hamiltonian.

CHAPTER VII

THE CRYSTAL FIELD

The Cubic Field

With H_o taken as the first three terms in (6.1) the next perturbation term arises from the cubic portion of the crystalline electrostatic field. Presumably the same field acts on each of the two electrons so that

$$V_c = \sum_{i=1,2} (V_c)_i \qquad (7.1)$$

As in the case of corundum it will be assumed that the cubic field has octahedral symmetry so that $(V_c)_i$ can be expanded about the trigonal axis as (18)

$$(V_c)_i = A_4^o \, r_1^4 \{Y_{4,0}(\theta_i,\varphi_i) + (10/7)^{\frac{1}{2}} [Y_{4,3}(\theta_i,\varphi_i) - Y_{4,-3}(\theta_i,\varphi_i)]\} . \qquad (7.2)$$

The operator (7.2) belongs to the O_h symmetry group and it is found from group theory that such an operator will partially remove the $(2L + 1)$-orbital degeneracy of the Russell-Saunders multiplets of H_o. Specifically, it is

found that the various terms decompose in the following way:

$$
\begin{aligned}
{}^3F &\rightarrow {}^3T_1 + {}^3T_2 + {}^2A_2 \\
{}^1D &\rightarrow {}^1T_2 + {}^1E \\
{}^3P &\rightarrow {}^3T_1 \\
{}^1G &\rightarrow {}^1T_1 + {}^1T_2 + {}^1E + {}^1A_1 \\
{}^1S &\rightarrow {}^1A_1
\end{aligned}
$$

Since group theory does not predict the order of the cubic field levels this must be obtained from other sources. One possible source for obtaining this information is from the optical spectrum. D. S. McClure has analyzed the spectrum for V^{+++}-doped corundum and his results are shown in the diagram of Fig. 1 (28). However, a difficulty arises with V_2O_3. This crystal has a black color and apparently is opaque to any optical absorption. Therefore, it can only be assumed that the energy diagram in V_2O_3 is the same as in the doped-corundum crystal.

For the magnetics problem only the two triplet terms need be considered. The ${}^3P$ term must be considered since it has the same symmetry as one of the symmetry components of ${}^3F$ and one can expect matrix elements of V_c connecting these two levels. This will cause some mixing between the ${}^3F$ and ${}^3P$ wave functions. A first-order degenerate perturbation may now be performed to obtain the energy of each level in terms of the cubic field parameter defined as

$$\beta = - \langle r^4 \rangle / 14(\pi)^{\frac{1}{2}} . \qquad (7.3)$$

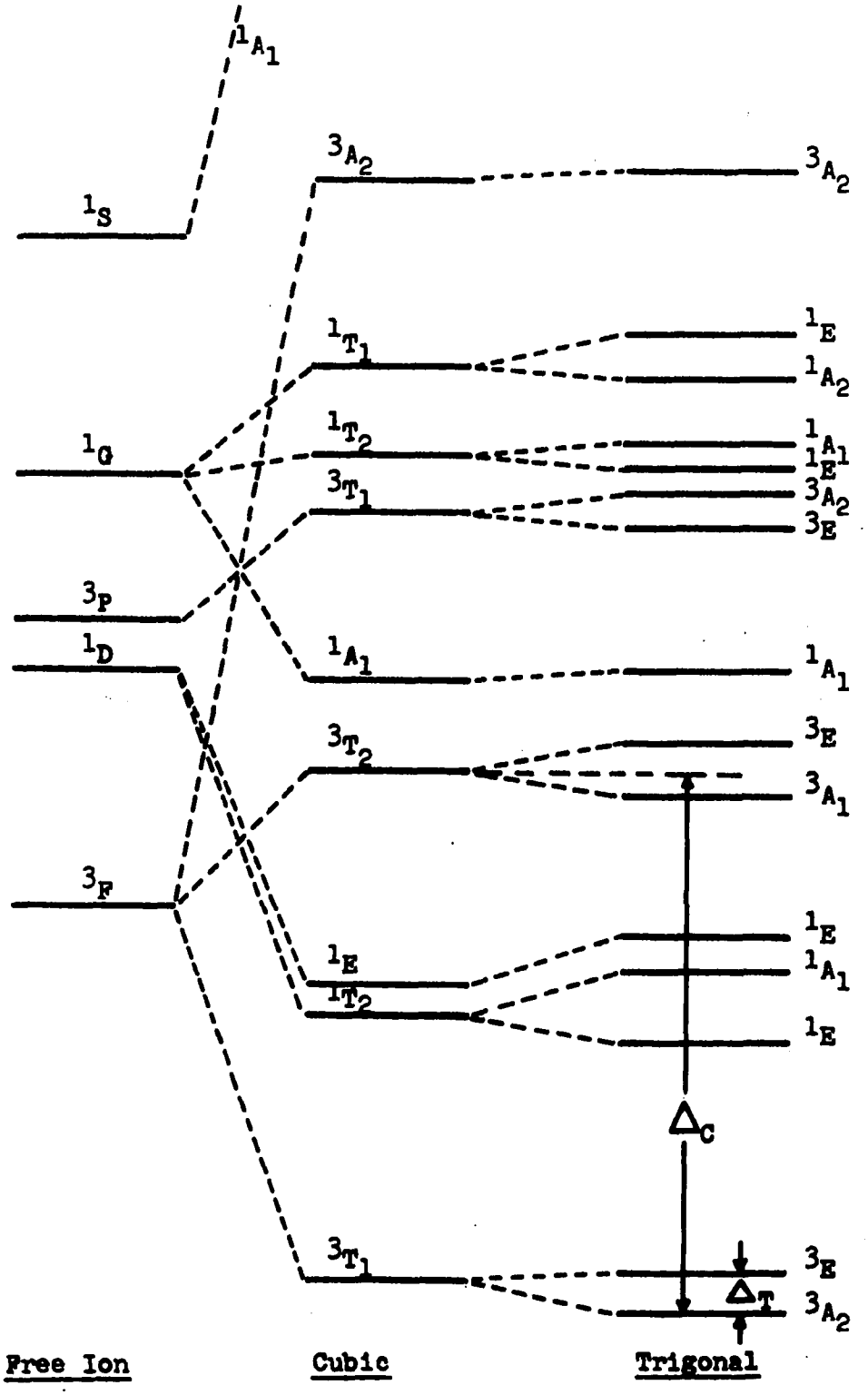


Figure 1. Energy Levels of V^{+++} in a Trigonal Field.

When this is done it is found that in the ^3F-manifold the secular equation contains one 3 x 3 block and two 2 x 2 blocks which can be diagonalized exactly. The matrix elements are given in Table VIII. In first-order, all matrix elements of V_c in the ^3P-manifold vanish. Upon solving the secular equation the energy eigenvalues associated with the various symmetry components of ^3F are found to be

$^3T_1(^3F)$: -9β, 3-fold orbital degeneracy
$^3T_2(^3F)$: 3β, 3-fold orbital degeneracy
$^3A_2(^3F)$: 18β, no orbital degeneracy.

TABLE VIII. MATRIX ELEMENTS OF V_c IN FREE-ION REPRESENTATION FOR ^3F.[a]

M_L	0	3	-3	1	-2	-1	2
0	6	$-3(10)^{\frac{1}{2}}$	$3(10)^{\frac{1}{2}}$				
3	$-3(10)^{\frac{1}{2}}$	3	0				
-3	$3(10)^{\frac{1}{2}}$	0	3				
1				1	$2(5)^{\frac{1}{2}}$		
-2				$2(5)^{\frac{1}{2}}$	-7		
-1						1	$-2(5)^{\frac{1}{2}}$
2						$-2(5)^{\frac{1}{2}}$	-7

[a]The free-ion M_L-value is given along the top and side, $M_S = 1$. The matrix elements are given in units of the cubic field parameter defined in (7.3).

The unitary transformation which gives the proper linear combination of free-ion wave functions in the cubic field representation is expressed as

$$\Psi_k = \sum_i A_{ki}\, \psi_i, \quad A^{-1}\, HA = E \tag{7.4}$$

where ψ_i are the free-ion functions. The cubic field functions Ψ_k are given in Table IX.

The ^3F-^3P mixing is obtained by solving the 6 x 6 secular equation resulting from matrix elements of V_c between the two $^3T_1$ levels. The equation factors into three identical 2 x 2 blocks with matrix elements

$$\begin{aligned} (^3P(^3T_1)\,|V_c|\,^3P(^3T_1)) &= \Delta_P \\ (^3P(^3T_1)\,|V_c|\,^3F(^3T_1)) &= -6\beta \\ (^3F(^3T_1)\,|V_c|\,^3F(^3T_1)) &= -9\beta\ . \end{aligned} \tag{7.5}$$

Where Δ_P is the energy separation between the ^3P and ^3F free-ion levels and is expressed in terms of the Slater-Condon parameters as

$$\Delta_P = 15\ F_2 - 75\ F_4\ . \tag{7.6}$$

Solving the 2 x 2 secular equation one obtains the following energy eigenvalues:

$$\begin{aligned} E[^3P(^3T_1)] &= \tfrac{1}{2}\,(\Delta_P - 9\beta) + \tfrac{1}{2}\,[(\Delta_P + 9\beta)^2 + 144\beta^2]^{\frac{1}{2}}\ , \\ E[^3F(^3T_1)] &= \tfrac{1}{2}\,(\Delta_P - 9\beta) - \tfrac{1}{2}\,[(\Delta_P + 9\beta)^2 + 144\beta^2]^{\frac{1}{2}}\ . \end{aligned} \tag{7.7}$$

TABLE IX. CUBIC FIELD FUNCTIONS OF ^3F AND ^3P.[a,b]

^3F

$$^3T_1: \quad \Psi(^3T_1,-,M_S) = -[\psi(^3F,-1,M_S) + (5)^{\frac{1}{2}}\psi(^3F,2,M_S)]/(6)^{\frac{1}{2}}$$

$$\Psi(^3T_1,0,M_S) = \frac{1}{3}\{2\psi(^3F,0,M_S) + (5/2)^{\frac{1}{2}}[\psi(^3F,3,M_S) - \psi(^3F,-3,M_S)]\}$$

$$\Psi(^3T_1,+,M_S) = -[\psi(^3F,1,M_S) - (5)^{\frac{1}{2}}\psi(^3F,-2,M_S)]/(6)^{\frac{1}{2}}$$

$$^3T_2: \quad \Psi(^3T_2,+,M_S) = [(5)^{\frac{1}{2}}\psi(^3F,1,M_S) + \psi(^3F,-2,M_S)]/(6)^{\frac{1}{2}}$$

$$\Psi(^3T_2,0,M_S) = [\psi(^3F,3,M_S) + \psi(^3F,-3,M_S)]/(2)^{\frac{1}{2}}$$

$$\Psi(^3T_2,-,M_S) = [(5)^{\frac{1}{2}}\psi(^3F,-1,M_S) - \psi(^3F,2,M_S)]/(6)^{\frac{1}{2}}$$

$$^3A_2: \quad \Psi(^3A_2,M_S) = \frac{1}{3}\{(5)^{\frac{1}{2}}\psi(^3F,0,M_S) - (2)^{\frac{1}{2}}[\psi(^3F,3,M_S) - \psi(^3F,-3,M_S)]\}$$

^3P

$$^3T_1: \quad \Psi(^3T_1,+,M_S) = \psi(^3P,1,M_S)$$

$$\Psi(^3T_1,0,M_S) = \psi(^3P,0,M_S)$$

$$\Psi(^3T_1,-,M_S) = \psi(^3P,-1,M_S)$$

[a] The notation ψ refers to the atomic wave functions of V^{+++}. The first symbol inside the parenthesis signifies the values of S and L, the second gives M_L, and the last, M_S. The cubic-field functions are denoted by Ψ with the first symbol inside the parenthesis for the symmetry properties and the second as an index of the components of the degenerate states. The free-ion functions ψ are constructed from linear combinations of the products of one-electron d orbitals. The Clebsch-Gordan coefficients are taken to be those given in Condon and Shortley.

[b] This table taken from Brumage, et al., Ref. 19.

The eigenfunctions may also be obtained from the proper unitary transformation but the mixing coefficients turn out to be very complicated functions of β and the eigenvalues (7.7). Since these coefficients are treated as parameters anyway they will be designated symbolically by simply writing

$$\varphi[^3F(^3T_1)] = a_1\Psi[^3F(^3T_1)] + a_2\Psi[^3P(^3T_1)] ,$$
$$\varphi[^3P(^3T_1)] = a_1\Psi[^3P(^3T_1)] - a_2\Psi[^3F(^3T_1)] . \qquad (7.8)$$

For V^{+++}-doped corundum a_1 and a_2 are taken to be (19)

$$a_1 = 0.959, \quad a_2 = 0.285 . \qquad (7.9)$$

These same values will be used for V_2O_3, since the magnetic susceptibility was found to be practically unaffected by a small variation in a_1 and a_2 at the temperatures of interest here.

This treatment of the cubic field has been given for the purpose of developing certain parameters which appear in the susceptibility expressions. In the absence of any optical data for V_2O_3 the energy differences and mixing coefficients which have been developed thus far will be taken to be the same as those found for corundum. That is, the corundum values for a_1, a_2, and Δ_C (see Fig. 1) will be used. For the vanadium alum $V(H_2O)_6^{3+}$, Hartman, et al. (25) found Δ_C to be 12,400 cm^{-1} and the $^3T_1$-$^3T_1$ spacing to be 26,200 cm^{-1}. The first of these represents a decrease of about 28% from its corundum value of 17,400 cm^{-1} (28), but the latter is

very nearly the same as its corundum value of 25,200 cm^{-1}. Neither of these represent unreasonable deviations from corundum and such an approximation is not expected to be any worse for pure V_2O_3. This is discussed more fully in Chapter XI where some rather heuristic evidence is given to show that such an approximation produces very little effect on the susceptibility. However, there are other parameters which do affect the susceptibility considerably. One of these is the splitting of the $^3T_1(^3F)$ level by a trigonal distortion in the crystal. This trigonal-field splitting will be developed in the next section.

The Trigonal Field

In the doped-corundum crystal it was found that many of the optical and magnetic properties could be accounted for by introducing a small trigonal correction to the predominantly cubic field. There is some experimental evidence for such a distortion in pure vanadium compounds possessing the same O_h symmetry as Al_2O_3. This is evident from the paramagnetic data by Carr and Foner which was taken from single crystals with the external magnetic field both parallel and perpendicular to the c-axis (20). While some anisotropy exists, it seems rather small compared with Al_2O_3 and it is known that the trigonal distortion is primarily responsible for this, at least in the crystal field approximation. Also calculations based on data for $V(H_2O)_6^{3+}$ which has O_h symmetry indicate a large trigonal distortion (18), (25).

The trigonal electrostatic field may also be expanded in spherical harmonics as

$$V_t = \sum_{i=1,2} [B_2^0 \, r_i^2 \, Y_{2,0}(\theta_i,\varphi_i) + B_4^0 \, r_i^4 \, Y_{4,0}(\theta_i,\varphi_i)]. \tag{7.10}$$

This potential function which possesses only axial symmetry can be regarded as a small perturbation to the Hamiltonian through V_c and further lifting of the orbital degeneracy of the cubic levels can be accomplished by another first-order degenerate calculation. The splitting of the cubic levels is again predicted by group theory to be (19)

$$^3T_1 \rightarrow {}^3E + {}^3A_2, \quad {}^3T_2 \rightarrow {}^3E + {}^3A_1 \tag{7.11}$$

with E, A_1, and A_2 unchanged. This splitting is also shown in Fig. 1 for the doped-corundum crystal.

A first-order degenerate perturbation may now be performed to find the two energy levels of $^3T_1(^3F)$ in terms of the trigonal-field parameters defined as

$$\begin{aligned} \tau &= - (5/\pi)^{\frac{1}{2}} B_2^0 \langle r^2 \rangle / 140 , \\ \upsilon &= - B_4^0 \langle r^4 \rangle / 14(\pi)^{\frac{1}{2}} . \end{aligned} \tag{7.12}$$

Using the mixed cubic-field functions of (7.8) as a basis the 3 x 3 secular equation is found to be diagonal. The non-vanishing matrix elements are

$$(^3F(^3T_1^{\pm}) \,|V_t|\, ^3F(^3T_1^{\pm})) = a_1^2 \, A + 2a_1a_2 \, B + a_2^2 \, C, \tag{7.13a}$$

$$(^3F(^3T_1^{o}) \,|V_t|\, ^3F(^3T_1^{o})) = a_1^2 \, D + 2a_1a_2 \, E + a_2^2 \, F, \tag{7.13b}$$

where

$$A = -\tau - 17\gamma\,, \quad B = -8\tau - 3\gamma\,, \quad C = -14\tau\,,$$
$$D = 2\tau + 13\gamma\,, \quad E = 16\tau - 8\gamma\,, \quad F = 28\tau\,, \tag{7.14}$$

The basis functions are still the cubic-field functions. Equation (7.13a) is energy of the ^3E trigonal level and is two-fold degenerate while (7.13b) is the energy of the $^3A_2$ level and is non-degenerate (orbitally). From the work of Brumage, et al. the trigonal parameters were found to be (19)

$$\tau \approx -7.3\ \text{cm}^{-1}, \quad \gamma \approx 38.5\ \text{cm}^{-1}\,. \tag{7.15}$$

These are expected to change considerably for V_2O_3.

A quantity which is important in the susceptibility theory is the energy difference between the two trigonal levels of $^3T_1(^3F)$. This trigonal-field splitting Δ_T is expressed in terms of the trigonal parameters and mixing coefficients as

$$\Delta_T = -a_1^2(3\tau + 30\gamma) - 2a_1a_2(24\tau - 5\gamma) - a_2^2\,42\tau\,. \tag{7.16}$$

Δ_T is a positive quantity for V_2O_3:Al_2O_3 since a_1 is much larger than a_2 and both trigonal parameters are found to be negative. This means that ^3E lies higher than $^3A_2$ and the same result is expected to hold for pure V_2O_3.

CHAPTER VIII

SPIN-ORBIT, EXCHANGE, AND MAGNETIC FIELD INTERACTIONS

The remaining terms in the Hamiltonian (6.1) represent magnetic effects. H_{s-o} represents an intraionic magnetic interaction between the spin and orbit of each electron, H_{ex} represents an interionic interaction associated with exchange effects, and the last term is the interaction of the cation with an external magnetic field. All of these will be combined into a single perturbation calculation for finding the energy but first each operator will be discussed separately.

Spin-Orbit Interaction

The interaction between the spin angular momentum and orbital angular momentum for two equivalent d-electrons is

$$H_{s-o} = \xi(\vec{\ell}_1 \cdot \vec{s}_1 + \vec{\ell}_2 \cdot \vec{s}_2) \ . \qquad (8.1)$$

This can be written as (32)

$$H_{s-o} = \frac{1}{2} \xi[(\vec{\ell}_1 + \vec{\ell}_2)\cdot(\vec{s}_1 + \vec{s}_2) + (\vec{\ell}_1 - \vec{\ell}_2)\cdot(\vec{s}_1 - \vec{s}_2)] \ . \qquad (8.2)$$

From the definition of angular momentum it is apparent that

$$\vec{L} = \vec{\ell}_1 + \vec{\ell}_2 \ , \quad \vec{S} = \vec{s}_1 + \vec{s}_2 \ . \tag{8.3}$$

In (8.3), $\vec{L}$ and $\vec{S}$ is the usual Russell-Saunders notation for total orbital and spin angular momentum, respectively. H_{s-o} can now be written as

$$H_{s-o} = \lambda \vec{L}\cdot\vec{S} + \lambda[(\vec{\ell}_1 - \vec{\ell}_2)\cdot(\vec{s}_1 - \vec{s}_2)] \ , \quad \lambda = \frac{1}{2}\xi \ . \tag{8.4}$$

The first term is the spin-orbit interaction expressed in the Russell-Saunders coupling scheme and the bracket term is a measure of the deviation from L-S coupling. The bracket term will connect levels having different symmetry in the Russell-Saunders scheme. It is not expected to affect the paramagnetic susceptibility a great deal since most of the contribution is from the $^3T_1(^3F)$ level. Therefore, it will be neglected and H_{s-o} will be taken as

$$H_{s-o} = \lambda \vec{L}\cdot\vec{S} \ . \tag{8.5}$$

In (8.4), λ is a function of the radial distance and the matrix elements will all contain this function averaged over the radial electronic distribution. It will be taken as a parameter in what follows.

Exchange Interaction

Since the neighboring cations in V_2O_3 are vanadium some exchange degeneracy exists between these ions. This exchange effect greatly alters the magnetic susceptibility and will be introduced here in a purely phenomonological

manner. The mechanism for this interaction is the same as in many other magnetic sesquioxides having the corundum structure (24). It is related to the extent and manner of the overlap of the electronic distributions centered on the different cations. The total exchange interaction is generally the sum of two distinctly different types of interactions, the strength of each type being related to the type of crystal symmetry and geometry and to the number of outer d-electrons associated with each cation (23). The cation-cation interactions arise from the direct overlap of the d-electron wave functions. In the corundum structure, two cases are distinguishable: the interaction between c-axis pairs of cations which share a common anion octahedral edge. The other type of contribution to the exchange effect is the cation-anion-cation interaction in which the d-wave functions overlap via an anion intermediary. In the corundum structure the interaction between c-axis pairs is much stronger than the other two but in this work no distinction will be made and some sort of averaged exchange will be deduced.

The Heisenberg exchange operator is used for the exchange interaction between a single cation and all of its neighbors. Thus, for a cation whose spin is $\vec{S}_i$ the interaction can be written as

$$H_{ex} = \vec{S}_i \cdot 2J \sum_{j \neq i} \vec{S}_j \ . \qquad (8.6)$$

This operator assumes that all the cations are equivalent and that J, the exchange integral, is the same for each. The summation is extended over all the cations in the crystal but most of the contribution will come from the first nearest cation neighbors and there are five of these for corundum. For identical cations, this summation can be replaced by the number of nearest neighbors times the average spin per cation. Letting z be the number of neighbors, (8.6) can be approximated by

$$H_{ex} = \vec{S} \cdot 2Jz\langle\vec{S}\rangle \equiv \vec{S} \cdot \vec{h} \qquad (8.7)$$

where the subscripts have been dropped since all the spins are the same and $\langle\vec{S}\rangle$ is the average spin per cation. The average is taken over the Boltzman temperature distribution and will be determined self-consistently later.

An internal molecular field is now introduced which has a magnitude of $2Jz\langle S\rangle$ and a direction which is parallel to the direction of an externally applied magnetic field. This should be the case if one neglects such things as anisotropic exchange and demagnetizing fields since the external field should cause the spin to precess about the direction of this applied field. Thus, for an external field in the z-direction the internal field $\vec{h}$ will split each triplet level into three components according to the M_s-value. The self-consistent determination of $\langle S\rangle$ will cause this exchange splitting to depend on temperature. The quantity 2Jz will be treated as a parameter to be determined from

experimental data. When treated this way, one cannot deduce how many neighbors participate in the exchange effect nor what kind of interactions contribute to the exchange integral.

Magnetic Field Interaction

The last term in the Hamiltonian (6.1) is the interaction between the spin and orbital magnetic moments with an externally applied magnetic field $\vec{H}$. Such an interaction depends upon the direction of the external field and the two cases of $\vec{H}$ parallel to the trigonal axis and perpendicular to this axis will be worked out. The interaction can be written in terms of the g-factor associated with spin only as

$$H = \mu_o(\vec{L} + g_s \vec{S})\cdot\vec{H} . \qquad (8.8)$$

The lowest trigonal level, $^3A_2$, is orbitally non-degenerate and its average orbital angular momentum vanishes in a first-order theory. This represents the quenching effect of the crystal field. That total quenching does not occur is evident from a second-order calculation in which matrix elements of $\vec{L}\cdot\vec{H}$ are found connecting different orbital levels in the crystal field. This deviation from total quenching produces an effective g-value which is slightly less than the spin-only value of 2.

The Energy Matrix

The eigenvalues and eigenfunctions of the Hamiltonian matrix up through the trigonal field have already been found.

Therefore, this much of the Hamiltonian may be regarded as the unperturbed Hamiltonian H_o and all the other terms as the perturbation. Then

$$H = H_o + H' \tag{8.9}$$

where

$$H' = \lambda \vec{L}\cdot\vec{S} + \vec{S}\cdot\vec{h} + \mu_o(\vec{L} + 2\vec{S})\cdot\vec{H} \ . \tag{8.10}$$

In (8.10) the spin-orbit and exchange interaction have been interchanged which makes no difference in a single perturbation calculation. H' will be carried through first- and second-order using as a representation the mixed cubic-field functions of Table IX and equation (7.8). The spin functions are the usual ones for triplet states.

The energy matrix is constructed using the $^3T_1(^3F)$ and $^3T_2(^3F)$ cubic field functions. The matrix elements are given in Table X. In this table α, α', α'' are related to the mixing coefficients as follows (19):

$$\alpha = (3/2)\ a_1^2 - a_2^2 \ , \quad \alpha' = (5/2)^{\frac{1}{2}}\ a_1 \ , \quad \alpha'' = a_1^2 - (3/2)\ a_2^2 \ . \tag{8.11}$$

The 18 x 18 matrix can be regarded as two 9 x 9 blocks, one for each of the cubic levels, with matrix elements connecting the two blocks. Furthermore, each of these blocks may be regarded as three 3 x 3 blocks with matrix elements connecting them. Within the $^3T_1$ block, one of the 3 x 3 blocks can be identified as belonging to the $^3A_2(^3T_1)$ trigonal level and the other two as belonging to the $^3E(^3T_1)$ trigonal level.

TABLE X. MATRIX ELEMENTS OF $H' = \lambda\vec{L}\cdot\vec{S} + \vec{s}\cdot\vec{h} + \mu_o(\vec{L} + g\vec{S})\cdot\vec{H}$ IN MIXED CUBIC REPRESENTATION[a,b]

(1) Within the $^3T_1(^3F)$ block

$(0,0|H'|0,\pm1) = (2)^{\frac{1}{2}}(h + gH_x)/2$

$(0,\pm1|H'|0,\pm1) = \pm(h + gH_z)$

$(\pm,0|H'|\pm,0) = \mp \alpha H_z$

$(+,\pm|H'|+,\pm1) = \mp \alpha\lambda - \alpha H_z \pm (h + gH_z)$

$(-,\pm1|H'|-,\pm1) = \pm\alpha\lambda + \alpha H_z \pm (h + gH_z)$

$(+,0|H'|+,\pm1) = (2)^{\frac{1}{2}}(h + gH_x)/2$

$(-,0|H'|-,\pm1) = (2)^{\frac{1}{2}}(h + gH_x)/2$

$(0,0|H'|\pm,\mp1) = -\alpha\lambda$

$(0,\pm1|H'|\pm,0) = -\alpha\lambda$

$(0,0|H'|\pm,0) = -(2)^{\frac{1}{2}}\alpha H_x/2$

$(0,\pm1|H'|+,\pm1) = -(2)^{\frac{1}{2}}\alpha H_x/2$

$(0,\pm1|H'|-,\pm1) = -(2)^{\frac{1}{2}}\alpha H_x/2$

(2) Between the $^3T_1(^3F)$ block and $^3T_2(^3F)$ block: $(^3T_1|H'|^3T_2)$

$(0,\pm1|H'|0,\pm1) = \pm(2)^{\frac{1}{2}}\alpha'\lambda + (2)^{\frac{1}{2}}\alpha' H_z$

$(0,\pm1|H'|\pm,0) = (2)^{\frac{1}{2}}\alpha'\lambda/2$

$(0,0|H'|\pm,\mp1) = (2)^{\frac{1}{2}}\alpha'\lambda/2$

$(0,0|H'|\pm,0) = \alpha' H_x/2$

$(0,\pm1|H'|+,\pm1) = \alpha' H_x/2$

$(0,\pm1|H'|-,\pm1) = \alpha' H_x/2$

$(+,\pm1|H'|+,\pm1) = (2)^{\frac{1}{2}}(\mp\alpha'\lambda - \alpha' H_z)/2$

$(-,\pm1|H'|-,\pm1) = (2)^{\frac{1}{2}}(\pm\alpha'\lambda + \alpha' H_z)/2$

$(0,0|H'|0,0)^c = (2)^{\frac{1}{2}}\alpha' H_z$

TABLE X -- CONTINUED

$(\pm,\mp1|H'|0,0) = \pm (2)^{\frac{1}{2}}\alpha'\lambda/2$

$(\pm,0|H'|0,\pm1) = \pm (2)^{\frac{1}{2}}\alpha'\lambda/2$

$(\pm,0|H'|\mp,\mp1) = - (2)^{\frac{1}{2}}\alpha'\lambda$

$(\pm,\pm1|H'|\mp,0) = - (2)^{\frac{1}{2}}\alpha'\lambda$

$(-,\pm1|H'|0,\pm1) = - \alpha' \mathcal{H}_x/2$

$(+,\pm1|H'|-,\pm1) = - \alpha' \mathcal{H}_x$

$(+,\pm1|H'|0,\pm1) = \alpha' \mathcal{H}_x/2$

$(-,\pm1|H'|+,\pm1) = - \alpha' \mathcal{H}_x$

$(\pm,0|H'|\mp,0) = - \alpha' \mathcal{H}_x$

$(\pm,0|H'|0,0) = \pm \alpha' \mathcal{H}_x/2$

(3) Within the $^3T_2(^3F)$ block

$(0,0|\vec{L}\cdot\vec{S}|\mp,\pm1) = \mp \frac{1}{2}$

$(0,\pm1|\vec{L}\cdot\vec{S}|\pm,0) = \pm \frac{1}{2}$

$(+,\pm1|\vec{L}\cdot\vec{S}|+,\pm1) = \pm \frac{1}{2}$

$(-,\pm1|\vec{L}\cdot\vec{S}|-,\pm1) = \pm \frac{1}{2}$

(4) Within the $^3T_1(^3P)$ block

$(0,0|\vec{L}\cdot\vec{S}|\mp,\pm1) = \alpha''$

$(+,\pm1|\vec{L}\cdot\vec{S}|+,\pm1) = \pm \alpha''$

$(-,\pm1|\vec{L}\cdot\vec{S}|-,\pm1) = \mp \alpha''$

$(0,\pm1|\vec{L}\cdot\vec{S}|\pm,0) = \alpha''$

---

[a]The two indices in the matrix elements correspond to the second and the third label of the wave functions in Table IX.

[b]Table taken from Brumage, et al., Ref. (19) except for elements containing h.

[c]This matrix element is omitted in the table of Brumage, et al., Ref. (19).

In the magnetics problem it is assumed that only the $^3A_2$ trigonal level is populated so it is necessary to obtain the eigenvalues of this small block only. To account for the elements connecting this block with all the others in the energy matrix, a second-order Van Vleck transformation is applied to reduce the relative magnitude of these connecting elements (27). For $\vec{H}$ in the z-direction (along trigonal axis) the 3 x 3 $^3T_1^o$-block reduces to three diagonal elements which are

$$(M_S=\pm1\,|M_S=\pm1) = \pm h \pm \mu_o g_\parallel H_z - \frac{2\alpha'^2\mu_o^2}{\Delta_C} H_z^2 - \frac{\alpha^2\lambda^2}{\Delta_T} - \frac{5}{2}\frac{\alpha^2\lambda^2}{\Delta_C}$$

$$(M_S=0\,|M_S=0) = -\frac{2\alpha^2\lambda^2}{\Delta_T} - \frac{\alpha'^2\lambda^2}{\Delta_C} - \frac{2\alpha'^2\mu_o^2}{\Delta_C} H_z^2 , \qquad (8.12)$$

and for $\vec{H}$ in the x-direction (perpendicular to trigonal axis),

$$(M_S=\pm1\,|M_S=\pm1) = -\frac{\alpha^2\lambda^2}{\Delta_T} - \frac{5}{2}\frac{\alpha'^2\lambda^2}{\Delta_C} - \mu_o\left(\frac{\alpha^2}{\Delta_T} + \frac{\alpha'^2}{\Delta_C}\right) H_x^2$$

$$(M_S=0\,|M_S=0) = -\frac{2\alpha^2\lambda^2}{\Delta_T} - \frac{\alpha'^2\lambda^2}{\Delta_C} - \mu_o^2\left(\frac{\alpha^2}{\Delta_T} + \frac{\alpha'^2}{\Delta_C}\right) H_x^2 \qquad (8.13)$$

$$(M_S=0\,|M_S=\pm1) = (h + \mu_o g_\perp H_x)/(2)^{\frac{1}{2}} .$$

In (8.12) and (8.13), Δ_C is defined in Fig. 1 and $g_\parallel$ and $g_\perp$ are defined as

$$g_\parallel = g_s - \frac{4\alpha'^2\lambda}{\Delta_C} , \quad g_\perp = g_s - \frac{\alpha'^2\lambda}{\Delta_C} - \frac{2\alpha^2\lambda}{\Delta_T} . \qquad (8.14)$$

Presumably, the exchange field $\vec{h}$ vanishes when the applied field is removed, especially in the paramagnetic region. This makes some of the terms in (8.12) and (8.13) field-independent and it is still possible, as in the doped-corundum case, to define the zero-field splitting as

$$\delta = \frac{\alpha^2\lambda^2}{\Delta_T} - \frac{3}{2}\frac{\alpha'^2\lambda^2}{\Delta_C} . \tag{8.15}$$

The two matrices obtained from (8.12) and (8.13) have three eigenvalues corresponding to three different energy levels and it is convenient to denote them by their jm-subscript, m = - 1,0,1. Since (8.12) is already diagonal the energy of each level for $\vec{H}$ parallel to the trigonal axis may be written down at once, in terms of the zero-field splitting, as

$$W_{jm} = W^o_{jm} + W^H_{jm} \tag{8.16}$$

where

$$W^o_{jm} = W^o_j + \delta S^2_{z_{jm}} - \frac{2\alpha^2\lambda^2}{\Delta_T} - \frac{\alpha'^2\lambda^2}{\Delta_C} , \tag{8.17}$$

$$W^H_{jm} = h\, S_{z_{jm}} + \mu_o\, g_{\parallel}\, H_z\, S_{z_{jm}} - \frac{2\alpha'^2}{\Delta_C}\mu_o^2 H_z^2 . \tag{8.18}$$

In (8.17), W^o_j is the energy associated with H_o in (8.9) and does not depend on the m-subscript. S_z is -1,0,1 depending on the m-value. The matrix of (8.13) can be diagonalized and the energy levels expressed in a similar way providing one assumes that the zero-field splitting is much larger

than the total magnetic energy, including the exchange energy. Although the exchange term will decrease the magnetic energy it is expected that δ will be slightly less in the pure crystal than in the dilute crystal because of the greater trigonal distortion. Nevertheless, this is not expected to alter the validity of such an assumption a great deal and it will be made in what follows. The energy levels of (8.13) are again expressed by (8.16) with (8.17) unchanged. However, for the perpendicular case (8.18) becomes

$$W^{H}_{jm} = -\mu_o^2 \left(\frac{\alpha^2}{\Delta_T} + \frac{\alpha'^2}{\Delta_C} \right) \mathcal{H}_x^2 - (1/\delta)(h + \mu_o g_\perp \mathcal{H}_x)^2 (1 - \frac{1}{2} S_{z_{jm}} - \frac{3}{2} S^2_{z_{jm}}) \, . \qquad (8.19)$$

All symbols in (8.19) have the same meaning as before.

The energy matrix for the $^3A_2(^3T_1)$ trigonal level has been reduced to diagonal form, at least approximately, and the energy of each magnetic level has been expressed in terms of the molecular exchange field h which still includes the unknown quantity $\langle S \rangle$. The next chapter is devoted to a self-consistent determination of this quantity.

CHAPTER IX

SELF-CONSISTENT DETERMINATION OF THE MOLECULAR FIELD

The determination of the molecular field should fulfill two intuitive requirements. First, in the paramagnetic region and in the absence of an applied field one could expect the molecular field to vanish since there is no axis of quantization for the spin system and the average spin per cation would be zero. Second, at very high temperature even with an applied field, the thermal energy would de-couple the spins, again causing the molecular field to vanish. Both of these requirements are met in the self-consistent method developed by Kanamori for FeO and CoO(26). This method neglects any distortion in the spin system by spin-orbit coupling and includes only first-order distortion by the applied field. In operator form, the spin per cation is obtained from (6.1) using (8.7) as

$$S_{op} = \frac{\partial H}{\partial (2Jz\langle S\rangle)} \tag{9.1}$$

and the spatial average is

$$S = \frac{\partial W_{jm}}{\partial (2Jz\langle S\rangle)} \cdot \tag{9.2}$$

The thermal average is then obtained using the Boltzman

distribution as

$$\langle S \rangle = \frac{\sum_{jm} \frac{\partial W_{jm}}{\partial(2Jz\langle S\rangle)} e^{-W_{jm}/kT}}{\sum_{jm} e^{-W_{jm}/kT}} . \qquad (9.3)$$

This may be simplified using (8.16) and assuming the magnetic energy is small compared to the thermal energy. This permits an expansion of the exponentials to give

$$\langle S \rangle \left[\sum e^{-W^{o}_{jm}/kT} - \frac{1}{kT} \sum W^{H}_{jm} e^{-W^{o}_{jm}/kT} \right]$$

$$= \sum \frac{\partial W_{jm}}{\partial(2Jz\langle S\rangle)} \left(1 - \frac{W^{H}_{jm}}{kT}\right) e^{-W^{o}_{jm}/kT} . \qquad (9.4)$$

For the parallel case, (9.4) with (8.17) and (8.18) gives

$$\langle S \rangle = - \frac{\mu_o g_{\parallel} \mathcal{H}_z}{kT} \frac{2e^{-\delta/kT}}{1 + 2e^{-\delta/kT} \frac{2Jz}{kT} \cdot 2e^{-\delta/kT}} \qquad (9.5)$$

Again if the zero-field splitting is much less than the thermal energy as well as 2Jz, (9.5) becomes

$$\langle S \rangle = - \frac{2}{3} \mu_o g_{\parallel} \mathcal{H}_z \frac{1}{kT + (2/3)(2Jz)} . \qquad (9.6)$$

The following equation defines the temperature dependence of (9.6).

$$\langle S \rangle \equiv - \mu_o g_{\parallel} \mathcal{H}_z C . \qquad (9.7)$$

It is obvious that (9.6) meets the requirement of vanishing applied field and the high temperature condition. The energy (8.18) can now be written as

$$W^{H}_{jm} = \mu_o g_{\parallel} (1 - 2JzC)H_z - (2\alpha'^2/\Delta_C) \mu_o^2 H_z^2 . \qquad (9.8)$$

As stated earlier, the exchange term decreases the magnetic energy as is evident from (9.8).

For the perpendicular case, (9.4) is again used with (8.17) and (8.19). No additional assumptions are needed, however second-order terms in the total magnetic energy and zero-field splitting must be retained. The previous assumptions are sufficient to reduce the original cubic equation in $\langle S \rangle$ to a simple linear form which can be solved immediately with the result

$$\langle S \rangle = - \frac{2}{3} \mu_o g_{\perp} H_x \frac{1}{kT + \frac{2}{3}(2Jz)} , \qquad (9.9)$$

or

$$\langle S \rangle \equiv - \mu_o g_{\perp} H_x C . \qquad (9.10)$$

This is the same as (9.7) except for the effective g-value. The energy (9.19) now becomes

$$W^{H}_{jm} = - \left[\frac{\alpha^2}{\Delta T} + \frac{\alpha'^2}{\Delta C} + \frac{g_{\perp}^2}{\delta} (1-2JzC)(1 - \frac{1}{2} S_{z_{jm}} - \frac{3}{2} S^2_{z_{jm}}) \right] \mu_o^2 H_x^2 \qquad (9.11)$$

Again the exchange term reduces the magnetic energy.

Both (9.8) and (9.11) represent the magnetic energy

for a single cation in an effective molecular field. In the susceptibility theory the total energy for the entire crystal is needed and a correction term in the susceptibility equation is needed because in the molecular field approximation the exchange interactions are counted twice. This is shown in the next chapter.

CHAPTER X

MAGNETIC SUSCEPTIBILITY

The classical expression for magnetic susceptibility

$$\chi = M/\mathcal{H} \ , \quad M = N\,\bar{m} \ , \tag{10.1}$$

where M is the total magnetization, $\mathcal{H}$ is magnetic field, $\bar{m}$ is the average magnetic moment per vanadium atom, and N is the number of vanadium atoms. According to Van Vleck, $\bar{m}$ is given by (35)

$$\bar{m} = \frac{\sum_{jm} m_{jm}\, e^{-W_{jm}/kT}}{\sum_{jm} e^{-W_{jm}/kT}} \tag{10.2}$$

with

$$m_{jm} = -\frac{\partial W_{jm}}{\partial \mathcal{H}} = -\frac{\partial W^{H}_{jm}}{\partial \mathcal{H}} \ . \tag{10.3}$$

The magnetic energy can be written as

$$W^{H}_{jm} = W'\mathcal{H} + W''\mathcal{H}^2 \ , \quad m_{jm} = -W' - 2W''\mathcal{H} \ . \tag{10.4}$$

The field-independent susceptibility is obtained by expanding the exponentials in (10.2), using (10.4), and neglecting any permanent moment. The result is

$$\chi = \frac{N \sum_{jm} \left[\frac{W'^2}{kT} - 2W'' \right] e^{-W^o_{jm}/kT}}{\sum_{jm} e^{-W^o_{jm}/kT}} \cdot \qquad (10.5)$$

Equation (10.5) is applied to both the parallel and perpendicular cases in the usual way. For $\vec{H}$ parallel to the trigonal axis the susceptibility is

$$\chi_{\parallel} = \frac{2}{3} \frac{N \mu_o^2}{k} \left\{ g_{\parallel}^2 \left[\frac{(1-2JzC)^2}{T} + \frac{3}{2} k(2Jz)C^2 \right] + \frac{6k\alpha'^2}{\Delta_C} \right\} . \qquad (10.6)$$

For $\vec{H}$ perpendicular to the trigonal axis the result is

$$\chi_{\perp} = \frac{2}{3} \frac{N \mu_o^2}{k} \left\{ g_{\perp}^2 \left[\frac{(1-2JzC)^2}{T} + \frac{3}{2} k(2Jz)C^2 \right] + \frac{3k\alpha^2}{\Delta_T} + \frac{3k\alpha'^2}{\Delta_C} \right\} . \qquad (10.7)$$

Both of these expressions apply only to the high-temperature region. For these temperatures, (10.6) and (10.7) are identical to the results for the doped-corundum problem except for the terms containing (2Jz). The second term in each square bracket is the correction term mentioned earlier. The contribution to the energy from exchange interaction only is found from (8.7), (9.7), (9.10) to be

$$W_{ex} = 2Jz\langle\vec{S}\rangle \cdot \langle\vec{S}\rangle$$

$$= 2Jz(\mu_o g_{\parallel,\perp} H_{z,x} C)^2$$

$$= W'' H^2 .$$

Now using (10.5) with $W' = 0$,

$$\chi_{ex} = -2NW'' = -2N(2Jz)(\mu_o\, g_{\parallel,\perp}\, C)^2$$

To avoid counting twice the contribution to the susceptibility from exchange, one-half of χ_{ex} is subtracted from the uncorrected susceptibility. Thus the correction term in (10.6) and (10.7) is established.

The tabulated susceptibility data for V_2O_3, over the range of temperatures of interest here, was published by J. Wucher in 1952 (37). This was for four different powder samples of V_2O_3 and the one which will be used here for comparison is the sample prepared at 1300°C since it is the one with the highest stoichiometric purity. Thus, it will be convenient to have an expression for the powder susceptibility. According to Van Vleck, this is given by (34)

$$\chi_P = \frac{1}{3}\chi_{\parallel} + \frac{2}{3}\chi_{\perp} \,. \tag{10.8}$$

Using (10.6) and (10.7) the result is

$$\chi_P = \frac{2}{3}\frac{N\mu_o^2}{k}\left\{ g_P^2\left[\frac{(1-2JzC)^2}{T} + \frac{3}{2}k(2Jz)C^2\right] + \frac{4k\alpha'^2}{\Delta_C} + \frac{2k\alpha^2}{\Delta_T}\right\} \tag{10.9}$$

where

$$g_P^2 = \frac{1}{3}g_{\parallel}^2 + \frac{2}{3}g_{\perp}^2 \,. \tag{10.10}$$

Equation (10.9) contains several unknown parameters, namely, g_P, $2Jz$, α', α, Δ_C, Δ_T. Normally the last four of

these can be determined from the optical spectrum but this is not possible for V_2O_3. Also, g_p is usually determined in the dilute crystal from the low-temperature data, but again this is not possible for V_2O_3 since it undergoes a crystallographic phase change at about 168°K. However, it is still possible to make some reasonable estimates of some of these parameters. In Fig. 2 equation (10.9) is compared with the experimental data of Wucher for several values of some of the parameters. In all the curves the values of α', α, Δ_c obtained from the dilute crystal are used. This choice will be discussed later. From Fig. 2 it is obvious that reasonably good agreement is obtained in the two different temperature regions but only with a different set of parameters. This is also discussed later.

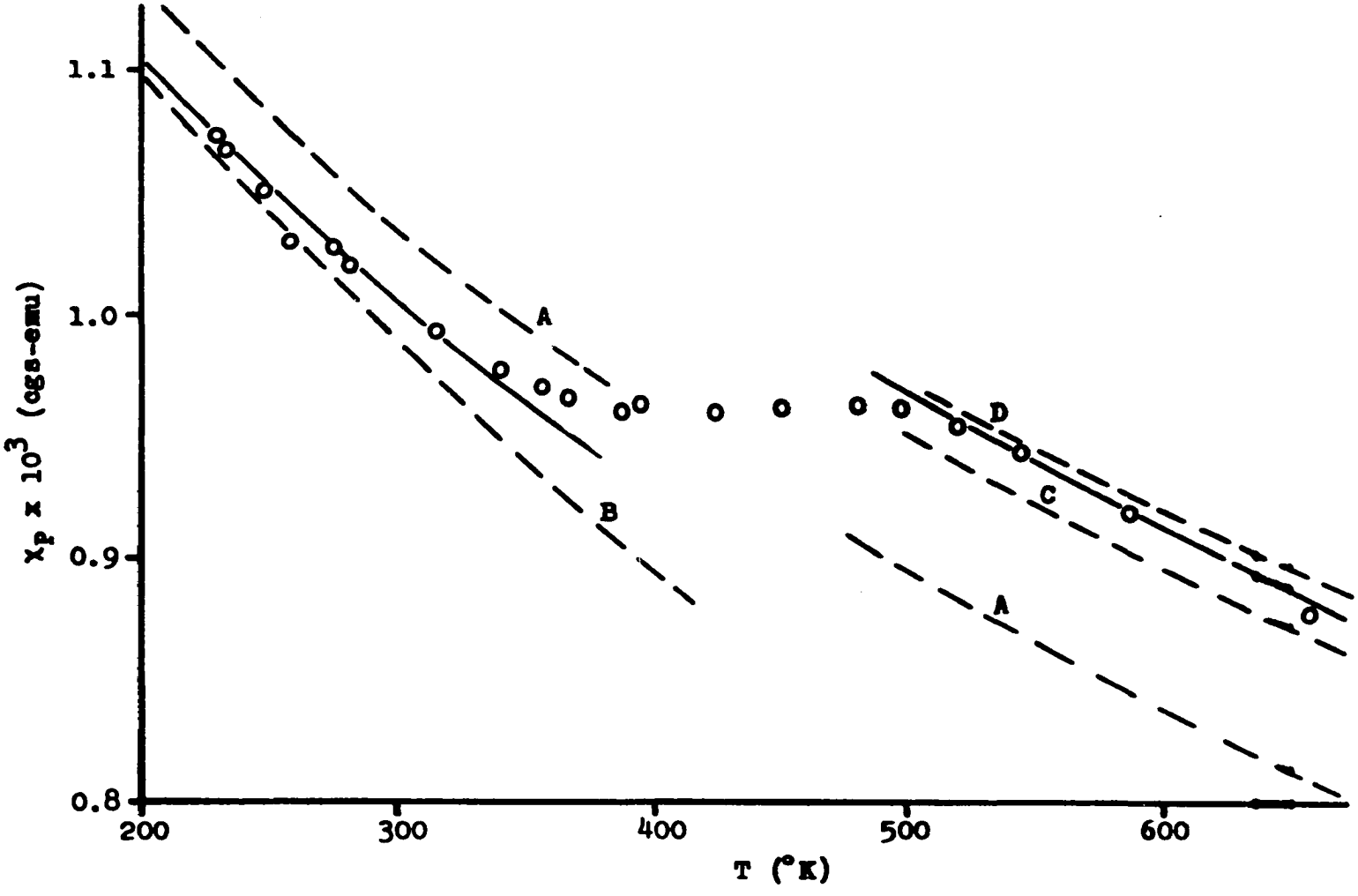


Figure 2. Powder Susceptibility (Per Vanadium Atom) vs. Temperature. Parameters for solid curve are given in text. For curve A, $2Jz = 770$, $\Delta_T = 2300$; curve B $2Jz = 720$, $\Delta_T = 2640$; curve C, $2Jz = 770$, $\Delta_T = 2100$; curve D, $2Jz = 790$, $\Delta_T = 2000$ (all in cm^{-1}). Circles are data from Ref. 37.

CHAPTER XI

DISCUSSION AND ANALYSIS OF RESULTS

In fitting the theoretical curve to the experimental data it was found that the magnitude of the susceptibility was mostly controlled by the temperature-independent term in (10.9) while the slope, or gentle curvature, was more sensitive to the exchange parameter, $2Jz$. This is shown by the various curves in Fig. 2. To justify using some of the parameters from the doped-corundum problem, a simple calculation was made in which first-order variations in the unknown parameters about their corundum values were permitted. These consisted of making the following replacements in (10.9) and (8.14):

$$\alpha \to \alpha + \epsilon \,, \quad \alpha' \to \alpha' + \epsilon' \,, \quad \lambda \to \lambda + \lambda'$$

$$\Delta_C \to \Delta_C - \delta' \,, \quad \Delta_T \to \Delta_T + \tau \,,$$

where all the variations are taken as positive quantities. After the replacements were made all appropriate terms were expanded through first-order in small quantities. To get an estimate of the sensitivity of χ_p to these variations, the following values (all in cm^{-1}) were then used:

$$\lambda' = 5 , \quad \delta' = 5000 , \quad \tau = 300 , \quad \epsilon = 0.134 \times 10^{-3} ,$$
$$\epsilon' = 7.9 \times 10^{-3} .$$

These produced a value for g_p approximately 2.8% larger than its corresponding corundum value but a value for the temperature-independent term in (10.9) which was about 20% smaller than its corundum value. Furthermore, the contribution from each of the variations could be isolated and for the same percentage variation in each of the parameters the contribution from the variation in Δ_T was at least one order of magnitude greater than any of the other variations. Thus, the corundum values seemed to be a reasonable estimate for λ, α, α', Δ_C for the purpose of fitting the susceptibility. The larger V-O distances in pure V_2O_3 should actually cause Δ_C to decrease from its corundum value of 17,400 cm^{-1} (28). In the case of $V(H_2O)_6^{3+}$, Δ_C was found to be 12,400 cm^{-1} (18). The ^3F-^3P spacing, λ, α, α' could also be expected to approach more closely their free-ion values.

The curves in Fig. 2 which best fit the experimental data are associated with the following set of parameters.

$200°K < T < 320°K$:

$$2Jz = 770 \text{ cm}^{-1} , \quad \Delta_T = 2410 \text{ cm}^{-1} , \quad g_p = 1.946$$

$500°K < T < 700°K$:

$$2Jz = 740 \text{ cm}^{-1} , \quad \Delta_T = 2100 \text{ cm}^{-1} , \quad g_p = 1.905$$

If only the five nearest neighbors participate equally in the exchange interactions, this would give $J = 77$ cm^{-1} and 74 cm^{-1}, respectively. The difference in these two values

is not considered significant in view of the molecular field approximation which has been used. Even the magnitudes themselves should be considered strictly as an empirical value.

In both temperature regions the value of Δ_T needed to fit the data is considerably larger than its corundum value of 1200 cm^{-1} (19). That V_2O_3 has more trigonal distortion than corundum is not unexpected since the lattice geometry is different. For chromium ions in ruby and in Cr_2O_3 the trigonal field was found to be so sensitive to the lattice geometry that ruby electric-effect constants could not be used in Cr_2O_3 magnetic calculations (17). In fact, for these two crystals, Foner's observations indicate that the trigonal field reverses sign and its magnitude decreases by 1/9 in going from ruby to Cr_2O_3 (22). Therefore, one should be cautious in relating any physical meaning to the large Δ_T obtained here although physical arguments could be proposed which would seem to support it, but these should also be applicable to Cr_2O_3 as well. The fact that two different values of Δ_T are needed to fit the two temperature regions appears to be in qualitative agreement with Goodenough's explanation of the high temperature transition (24). According to Goodenough, as the temperature is decreased through the transition region, homopolar c-axis bonding sets in and the cations move toward their c-axis mates away from the center of symmetry of their respective interstices

causing an increase in the c/a ratio for the crystal. It is possible that such displacement of the cations away from their centers of symmetry could produce a change in the trigonal splitting.

The results presented so far have been based on a one-ion approximation where the electrical and magnetic environment of the crystal has been treated phenomenologically as a perturbation to the energy levels of a single cation. However, because of the pairing of cations along the c-axis in the corundum structure it is possible to treat the exchange interactions between the pair exactly and use the effective internal magnetic field to describe the effect on the pair of the "off-axis" cations. This possibility is explored in the following chapter.

CHAPTER XII

THE COUPLED PAIR MODEL

The coupled pair model treats the exchange interactions between the c-axis pairs exactly and the resulting homonuclear diatomic molecule is coupled to the remainder of the magnetic lattice by an effective internal magnetic field, just as in the one-ion approximation. Such a model has been applied to Cr_2O_3 below the Neel temperature but has not been extended to the paramagnetic region (31). Generally, the low temperature data is used to determine if the dominant magnetic interactions are antiferromagnetic or ferromagnetic in nature but because of the anomalous properties of V_2O_3 near the low temperature transition this is not possible. Therefore, there is no a priori reason to assume one or other so both cases are treated separately.

Since the orbital contribution to the magnetic susceptibility is a second-order effect it is possible to study the qualitative features of the model by considering a pure spin system. The orbital contribution will be discussed later.

The Antiferromagnetic-Ferromagnetic Model

The direct exchange interaction between the c-axis

pair is assumed to be antiferromagnetic while the coupling of the pair to the effective field is ferromagnetic. It is also assumed that the former is much stronger than the latter. This model will be referred to as the AF-F model. A more precise formulation follows.

Consider a two-layer structure where each layer contains one of the cations belonging to a c-axis pair. Let a and b be indices which label the two layers and i and j be indices associated with the cations within a layer. Then the Hamiltonian for the two-layer spin system in an external magnetic field is

$$H = \sum_i J\, \vec{S}_i^a \cdot \vec{S}_j^b - \sum_{i \neq j} 2J'(\vec{S}_i^a \cdot \vec{S}_j^a + \vec{S}_i^b \cdot \vec{S}_j^b) + 2\,\mu_o \sum_i \vec{S}_i^a \cdot \vec{\mathcal{H}} + 2\,\mu_o \sum_i \vec{S}_i^b \cdot \vec{\mathcal{H}} \,. \tag{12.1}$$

In (12.1) the signs have been chosen so that both J and J' are positive exchange parameters for the AF-F formulation. The 2 appearing in the last two terms of (12.1) is the electron g-factor which should not be altered in the absence of any orbital contribution. Since all cations are assumed to be in the triplet spin state, $S_i = S_j = 1$. It is possible to express (12.1) in terms of the total spin as

$$H = J \sum_i \vec{S}_i^a \cdot \vec{S}_i^b - J' \sum_{i \neq j} (\vec{S}_i \cdot \vec{S}_j + \vec{S}_i' \cdot \vec{S}_j') + 2\,\mu_o \sum_i \vec{S}_i \cdot \vec{\mathcal{H}} \tag{12.2}$$

where $$\vec{S}_i = \vec{S}_i^a + \vec{S}_i^b \,, \quad \vec{S}_i' = \vec{S}_i^a - \vec{S}_i^b \,. \tag{12.3}$$

In (12.2) it has been assumed at the outset that J and J' are independent of all indices.

Further simplication can be obtained by considering only the ferromagnetic terms. These are written in (12.1) in terms of the strong field coupling scheme whereas in (12.2) the first part can be recognized as the weak field coupling scheme (analogous to Russell-Saunders coupling in spin-orbit interactions) and the second part may be considered as a correction to the weak field scheme. This correction term may be analyzed by recognizing $\vec{S}_i'$ as being a so called T-vector with respect to the total spin $\vec{S}_i$, and similarly for $\vec{S}_j'$ (see Ref. 4). Then in the $S^aS^bSM_S$ representation the correction term will connect states for which $\Delta S_i = \Delta S_j = 0 \pm 1$ but either of these combinations represents a second-order effect since i is never equal to j in this term. Therefore, the correction term in (12.2) will be neglected and the weak field coupling scheme can now be used.

The Hamiltonian for the coupled pair of i^{th} cations can now be written, after dropping the i-subscript, as

$$H = J\,\vec{S}^a \cdot \vec{S}^b - J'\vec{S} \cdot \sum_j \vec{S}_j + 2\,\mu_o\,\vec{S} \cdot \vec{H} \,. \tag{12.4}$$

Since all pairs should be identical the j-summation can be replaced by the number of "off-axis" neighbors to the pair times the average spin for the coupled system. Thus,

$$H = J\,\vec{S}^a \cdot \vec{S}^b - \vec{S} \cdot J'z\,\langle\vec{S}\rangle + 2\,\mu_o\,\vec{S} \cdot \vec{\mathcal{H}}\,. \qquad (12.5)$$

This Hamiltonian serves as the starting point for a two-step successive perturbation treatment.

It is easy to show that the first term in (12.5) is diagonal in the weak field representation and the energy levels, apart from a constant term, are given by

$$W_S = \tfrac{1}{2}JS(S + 1) \qquad (12.6)$$

where the total spin S takes the values 2, 1, 0. The basis functions are Clebsch-Gordan combinations of the single ion triplet spin functions and are given in Table XI. These are used to treat the next two terms in (12.5).

At this point it should be noted that the Hamiltonian (12.5) contains no anisotropic terms and it is only necessary to treat a single direction, say the z-direction. Since the ferromagnetic interaction now behaves as an effective magnetic field the energy will depend only on S_z and similarly for the last term in (12.5). Therefore, the energy of each level can be written down immediately as

$$W_{SM_S} = \tfrac{1}{2}JS(S + 1) - (J'z\,\langle S\rangle - 2\,\mu_o\,\mathcal{H})S_z. \qquad (12.7)$$

The effective molecular exchange field is determined in the same way as in Chapter IX. Using (9.1), (9.2), and (9.3) the result is

$$\langle S\rangle = 2\,\mu_o\,\mathcal{H}\,C \qquad (12.8)$$

where

TABLE XI. CLEBSCH-GORDAN COMBINATIONS OF TRIPLET SPIN FUNCTIONS[a]

S = 2:	$S_{22} = S_+^a S_+^b$
	$S_{21} = (S_0^a S_+^b + S_+^a S_0^b)/\sqrt{2}$
	$S_{20} = (S_+^a S_-^b + 2S_0^a S_0^b + S_-^a S_+^b)/\sqrt{6}$
	$S_{2-1} = (S_0^a S_-^b + S_-^a S_0^b)/\sqrt{2}$
	$S_{2-2} = S_-^a S_-^b$
S = 1:	$S_{11} = (S_0^a S_+^b - S_+^a S_0^b)/\sqrt{2}$
	$S_{10} = (S_+^a S_-^b - S_-^a S_+^b)/\sqrt{2}$
	$S_{1-1} = (S_0^a S_-^b - S_-^a S_0^b)/\sqrt{2}$
S = 0:	$S_{00} = (S_+^a S_-^b - S_0^a S_0^b + S_-^a S_+^b)/\sqrt{3}$

[a]The subscripts on the coupled spin functions give the SM_S values and those on the one-ion functions are the M_S values corresponding to +1, 0, -1.

$$C = \frac{C'}{1 + J'zC'} = C', \quad \frac{1}{kT} \quad \frac{2e^{-J/kT} + 10e^{-3J/kT}}{1 + 3e^{-J/kT} + 5e^{-3J/kT}} \tag{12.9}$$

Using (12.8), W_{SM_S} can be written as

$$W_{SM_S} = \tfrac{1}{2}JS(S + 1) + (1 - J'zC)^2 \mu_o \mathcal{H} S_z \tag{12.10}$$

which has the form

$$W_{SM_S} = W_S^o + W'_{SM_S} \mathcal{H} . \tag{12.11}$$

The magnetic susceptibility is obtained from (10.5) with W" set equal to zero. The result is

$$\chi = 4N \mu_o^2 (1 - J'zC)^2 C' \tag{12.12}$$

where N now represents the number of pairs and is equal to the number of V_2O_3 molecules in the crystal. Equation (12.12) must again be corrected for double-counting in the molecular field approximation. The procedure is the same as in Chapter X with the result that

$$\chi = 4N \mu_o^2 (1 - 2J'zC) C \tag{12.13}$$

with C given by (12.9). The exchange parameters J and J'z contained in (12.13) can now be adjusted in an effort to fit the experimental data.

In Figure 3 the pair susceptibility is plotted as a function of temperature for various choices of the two parameters. Several things are obvious from the figure. First, all curves have a tendency to approach each other at

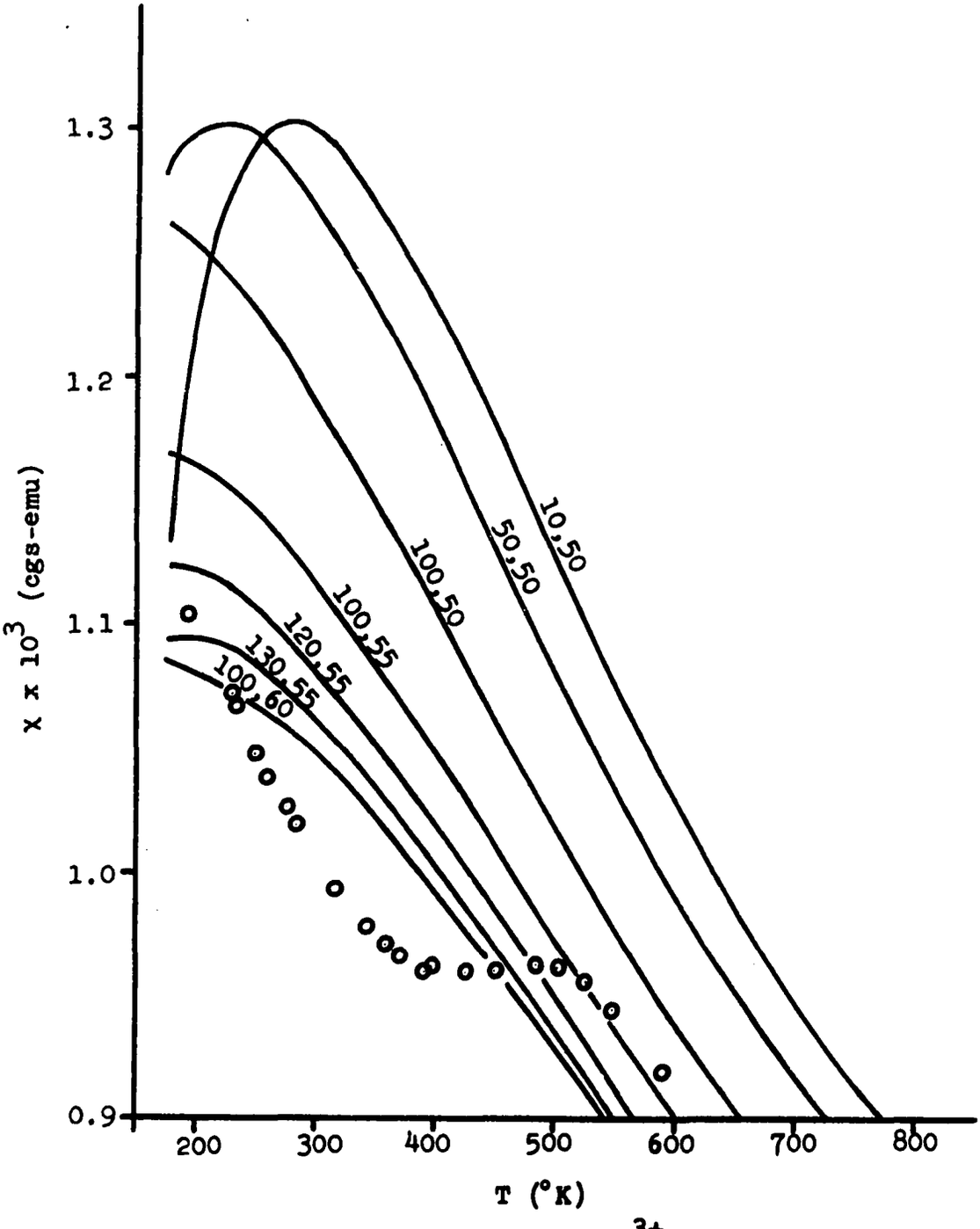


Figure 3. Pair Susceptibility (per V^{3+} ion) vs. Temperature for the AF-F Model. Numbers are the J, J'z values, respectively (all in cm^{-1}). Circles are data from Ref. 37.

the higher temperatures as one would expect. Second, it appears that the position of the Neel point depends more strongly on J while at the lower temperatures the absolute value of the susceptibility depends more strongly on J'z. The high temperature transition is still not accounted for and the J = 130 cm^{-1}, J'z = 55 cm^{-1} curve was about the best fit of the data that could be obtained. However, as stated earlier, only the qualitative features of the model were to be explored and from this viewpoint reasonable agreement is obtained, especially above 500°K.

The Ferromagnetic-Antiferromagnetic Model

Because of the absence of any conclusive evidence for taking the direct exchange interaction to be antiferromagnetic it is reasonable to explore the possibility that it may indeed be ferromagnetic. This is referred to as the F-AF model. Everything is the same as in the AF-F model except for the signs on the exchange parameters. However, this difference is enough to change the susceptibility expression considerably. The energy of each level can be written down at once as

$$W_{SM_S} = -\tfrac{1}{2}JS(S+1) + (J'z\langle S\rangle + 2\,\mu_o\,\mathcal{H})S_z \,. \qquad (12.14)$$

The same procedure is now used to determine the exchange field with the result

$$\langle S\rangle = -2\,\mu_o\,\mathcal{H}\,C \qquad (12.15)$$

where

$$C = \frac{C'}{1 + J'zC'}, \qquad C' = \frac{1}{kT} \frac{2e^{J/kT} + 10e^{3J/kT}}{1 + 3e^{J/kT} + 5e^{3J/kT}} . \tag{12.16}$$

Substituting (12.15) into (12.14) gives

$$W_{SM_S} = -\tfrac{1}{2}JS(S + 1) + (1 - J'zC)2\,\mu_o\,\mathcal{H}\,S_z . \tag{12.17}$$

Thus, changing the signs on the exchange parameters has the effect of inverting the exchange levels, placing the S = 2 level lowest.

Equation (10.5) again gives the magnetic susceptibility which is the same as (12.12) but with C and C' given by (12.16). However, because of the change in sign on J' the molecular field correction term changes sign and this causes the second term in (12.13) to drop out. The result is simply

$$\chi = 4N\,\mu_o^2\,C \tag{12.18}$$

where again N is the number of pairs and C is given by (12.16).

The pair susceptibility for this case is plotted in Figure 4 and on a larger scale in Figure 5 for various choices of the exchange parameters. All the curves again approach each other at the higher temperatures and tend towards infinity at the lower temperatures. Such behavior is also to be expected since at high temperatures the molecular field vanishes and the thermal energy is sufficient to decouple the pair thus "washing out" the direct exchange

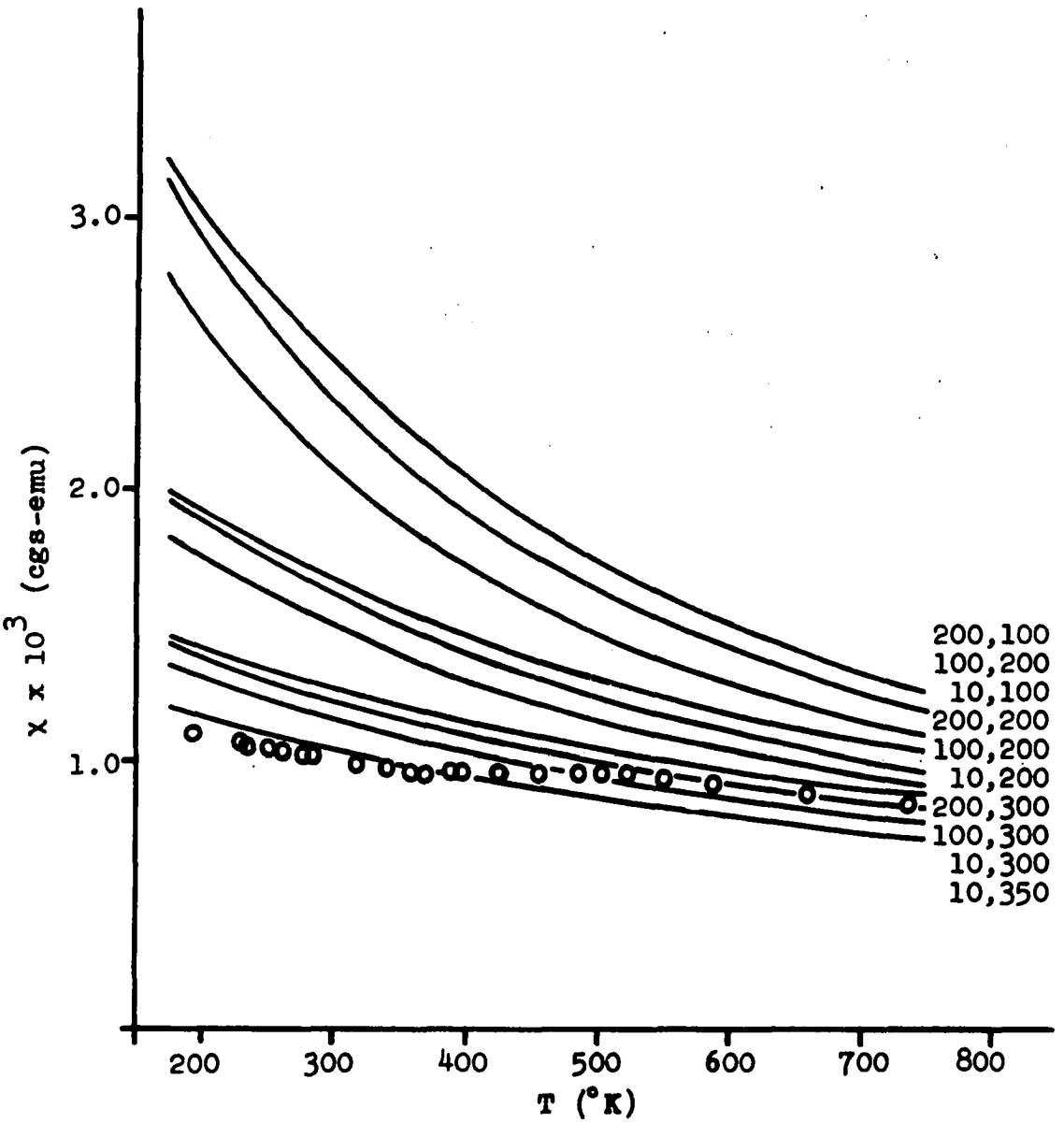


Figure 4. Pair Susceptibility (per V^{3+} ion) vs. Temperature for the F-AF Model. The first number in each pair is the J value and the second is the J'z value (all in cm^{-1}). Circles are data from Ref. 37.

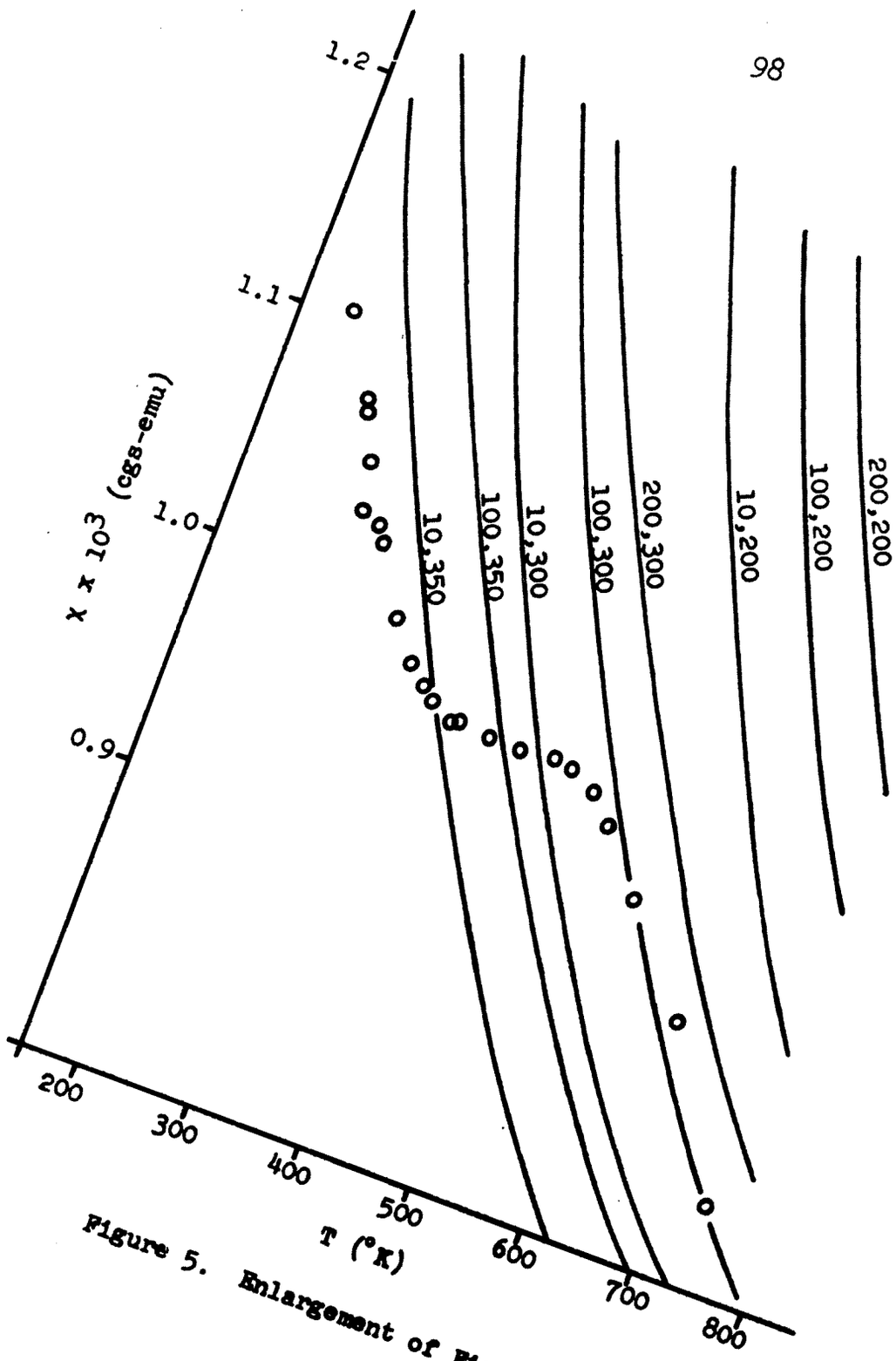


Figure 5. Enlargement of Figure 4

dependence. This is also true for the AF-F model in this temperature region. At the lower temperatures more magnetic ions reside in the S = 2 ground level which has a non-vanishing magnetic moment. Thus, as the population of this level increases the susceptibility should increase as the graphs indicate. On the other hand, the high temperature transition is still not predicted but there appears more hope of obtaining a satisfactory fit of the data in the two regions above and below this transition using two different sets of parameters. However, this is not regarded by any standards as being conclusive evidence that the dominant exchange interactions are ferromagnetic but merely suggests that, in the absence of low temperature data, some caution should be exercised in making an a priori assumption about the nature of the interactions.

The Orbital Contribution

The spin-only model is based on the assumption that the trigonal field splitting for each magnetic ion is infinite. This means that the upper trigonal levels of Figure 1, which give rise to the orbital effect, never get populated, thus eliminating any anisotropy and rendering the zero-field splitting meaningless. Since it is known that a small amount of anisotropy exists in V_2O_3 (24), it is worthwhile to derive the susceptibility expressions taking into account a large but finite trigonal splitting. To demonstrate the effect, the AF-F assumption will be made.

The Hamiltonian for the pair may be written down at once as

$$H = H_o^a + H_o^b + V_c^a + V_c^b + V_t^a + V_t^b + J\vec{S}^a \cdot \vec{S}^b + \lambda\vec{L}^a \cdot \vec{S}^a + \lambda\vec{L}^b \cdot \vec{S}^b$$
$$+ \mu_o\vec{L}^a \cdot \vec{H} + \mu_o\vec{L}^b \cdot \vec{H} + (\mu_o g\,\vec{H} - \vec{h}_a) \cdot \vec{S}^a$$
$$+ (\mu_o g\,\vec{H} - \vec{h}_b) \cdot \vec{S}^b \qquad (12.19)$$

where $\vec{h}_a = J'z\langle\vec{S}^a\rangle$ and similarly for $\vec{h}_b$. Because of the antiferromagnetic coupling between layers a and b, $\vec{h}_a$ and $\vec{h}_b$ should have the same magnitude but opposite directions, however, this will be accounted for by using the coupled spin representation. In Figure 1, the $^3T_2$ cubic level will be neglected but each ion in the pair may be in either of the two trigonal levels belonging to $^3T_1$. For each of these levels the individual spin system may be in any one of three exchange levels produced by the direct exchange term and corresponding to a <u>total</u> spin of 2, 1, 0. For the AF-F model, the S = 0 exchange level lies lowest. Thus the possible orbital assignments are $A_2^aA_2^b$, $A_2^aE^b$, $E^aA_2^b$, E^aE^b. The two-fold orbital degeneracy of the E level causes the secular equation to be quite large but the E^aE^b orbital pair level may be dropped since it does not combine magnetically with the $A_2^aA_2^b$ ground level. This results from the complete orthogonality of the orbital functions for these two levels. Also, the $A_2^aE^b$ and $E^aA_2^b$ levels both lie, in energy, a distance Δ_T above $A_2^aA_2^b$ and it is the interaction of these levels

with the ground level which must be incorporated into the susceptibility.

A secular equation is set up in the usual way for the operator (12.19) using, as a basis set, the orbital functions in Table IX mixed according to (7.8) and the spin functions of Table XI. Because of the directional effects, this must now be done for the external field in the z-direction and again for the field in the x-direction. For each case the elements of the secular equation are combinations of those in the first block of Table X. The procedure is now the same as for the one-ion approximation. That is, a Van Vleck transformation is used to reduce the size of the matrix elements connecting the $A_2^a A_2^b$ level with the higher level. Ordinary second-order perturbation is then used to get the energy of each SM_S level in the $A_2^a A_2^b$ block. Assigning zero energy to the S = 0 level gives:

for $\mathcal{H} = \mathcal{H}_z$:

$$W_{00} = (8/3)\delta$$
$$W_{10} = J + (1/2)\delta$$
$$W_{1\pm1} = J + (3/2)\delta \pm (\mu_o g_{\parallel} \mathcal{H}_z - h)$$
$$W_{20} = 3J + (5/3)\delta$$
$$W_{2\pm1} = 3J + (3/2)\delta \pm (\mu_o g_{\parallel} \mathcal{H}_z - h)$$
$$W_{2\pm2} = 3J + \delta \pm 2(\mu_o g_{\parallel} \mathcal{H}_z - h),$$

for $\mathcal{H} = \mathcal{H}_x$:

$$W_{00} = (8/3)\delta - (2\alpha^2/\Delta_T)\, \mu_o^2\, \mathcal{H}_x^2$$
$$W_{10} = J + (1/2)\delta - (2\alpha^2/\Delta_T)\, \mu_o^2\, \mathcal{H}_x^2 - (\mu_o g_{\perp}' \mathcal{H}_x - h)^2/\delta$$

$$W_{1\pm1} = J + (3/2)\delta - (2\alpha^2/\Delta_T)\,\mu_o^2\,\mathcal{H}_x^2 + (\mu_o\, g_\perp'\,\mathcal{H}_x - h)^2/(2\delta)$$

$$W_{20} = 3J + (5/3)\delta - (2\alpha^2/\Delta_T)\,\mu_o^2\,\mathcal{H}_x^2 + 18(\mu_o\, g_\perp\,\mathcal{H}_x - h)^2/\delta$$

$$W_{2\pm1} = 3J + (3/2)\delta - (2\alpha^2/\Delta_T)\,\mu_o^2\,\mathcal{H}_x^2 - 7(\mu_o\, g_\perp\,\mathcal{H}_x - h)^2(2\delta)$$

$$W_{2\pm2} = 3J + \delta - (2\alpha^2/\Delta_T)\,\mu_o^2\,\mathcal{H}_x^2 - 2(\mu_o\, g_\perp\,\mathcal{H}_x - h)^2/\delta\ .$$

The subscripts on W above are the SM_S values and α is the same as in the one-ion case. The zero-field splitting δ and the g-values are given by

$$\delta = -2\alpha^2\lambda^2/\Delta_T\ , \quad g_\parallel = g_S = 2\ ,$$

$$g_\perp' = g_S - \alpha^2\lambda/\Delta_T\ , \quad g_\perp = g_S - 2\alpha^2\lambda/\Delta_T\ .$$

It should be pointed out that the zero-field splitting is defined as a negative number here and is twice as large as the corresponding quantity for the one-ion case.

Using the above energies and (9.3) the molecular field can again be determined self-consistently with the result, for the z-direction, being

$$\langle S\rangle = \mu_o\, g_\parallel\,\mathcal{H}_z\, C_\parallel\ , \quad C_\parallel = \frac{C'}{1 + J'zC'} \qquad (12.20)$$

with

$$C' = \frac{1}{kT}\left[\, 2e^{-3\delta/2kT}\left(e^{-J/kT} + e^{-3J/kT}\right) + 8e^{-(3J+\delta)/kT}\,\right]/B$$

and

$$B = e^{-8\delta/3kT} + 2e^{-3\delta/2kT}(e^{-J/kT} + e^{-3J/kT})$$

$$+ e^{-(J + \delta/2)/kT} + e^{-3J/kT}(2e^{-\delta/kT} + e^{-5\delta/3kT}) .$$

Equation (10.5) again gives the susceptibility with W" set to zero. Thus,

$$\chi_{\parallel} = N \mu_o^2 g_{\parallel}^2 (1 - J'zC_{\parallel})C_{\parallel} . \qquad (12.21)$$

After correcting for double-counting the final expression is

$$\chi_{\parallel} = N \mu_o^2 g_{\parallel}^2 (1 - 2J'zC_{\parallel})C_{\parallel} . \qquad (12.22)$$

Again, N must be the number of pairs.

For the x-direction the procedure is the same but the actual calculation is slightly more complicated because of the two types of g-factors which appear in the energy expressions. After using (9.3), the terms which remain quadratic in magnetic energy are neglected just as in the one-ion case. This allows the molecular field to be written as

$$\langle S \rangle = \mu_o H_x C_{\perp} , \quad C_{\perp} = \frac{2}{\delta} \frac{g_{\perp}' C_2 + g_{\perp} C_3}{C_1 + 2J'z(C_2 + C_3)/\delta} \qquad (12.23)$$

with

$$C_1 = B$$

$$C_2 = e^{-J/kT}(e^{-\delta/2kT} - e^{-3\delta/2kT}) ,$$

$$C_3 = e^{-3J/kT}(4e^{-\delta/kT} + 14e^{-3\delta/2kT} - 18e^{-5\delta/3kT}) .$$

The susceptibility is again given by (10.5) with W' set to

zero. The result, after the molecular field correction, is

$$\chi_\perp = \frac{2N\mu_o^2}{\delta}\left[\frac{(g_\perp' - J'zC_\perp)^2C_2 + (g_\perp - J'zC_\perp)^2C_3}{C_1}\right.$$

$$\left. - \frac{\delta}{2}J'zC_\perp^2 + \frac{2\alpha^2\delta}{\Delta_T}\right]. \qquad (12.34)$$

The powder (or polycrystalline) susceptibility is given by substituting (12.22) and (12.24) into (10.8).

The pair susceptibility including the orbital effect is plotted in Fig. 6 and Fig. 7. It is obvious that the curves do not fit the experimental data very well but something new has appeared, and that is the high temperature non-cooperative transition which was one of the objectives of the calculation. Before giving a physical explanation for the formation of this transition it is convenient, first, to observe some of the more gross features of the graphs. By comparing corresponding curves in the two figures, one can see that a large change in the trigonal field splitting does not alter the curvature very much but only shifts all curves vertically. Therefore, adjustment of this parameter could possibly be used to obtain the right order of magnitude. To obtain the proper slope for the experimental data a small J'z is necessary but it is obvious that decreasing this parameter shifts the transition off to the left of the graphs. In order to obtain better quantitative results for V_2O_3 more flexibility in the model must be allowed.

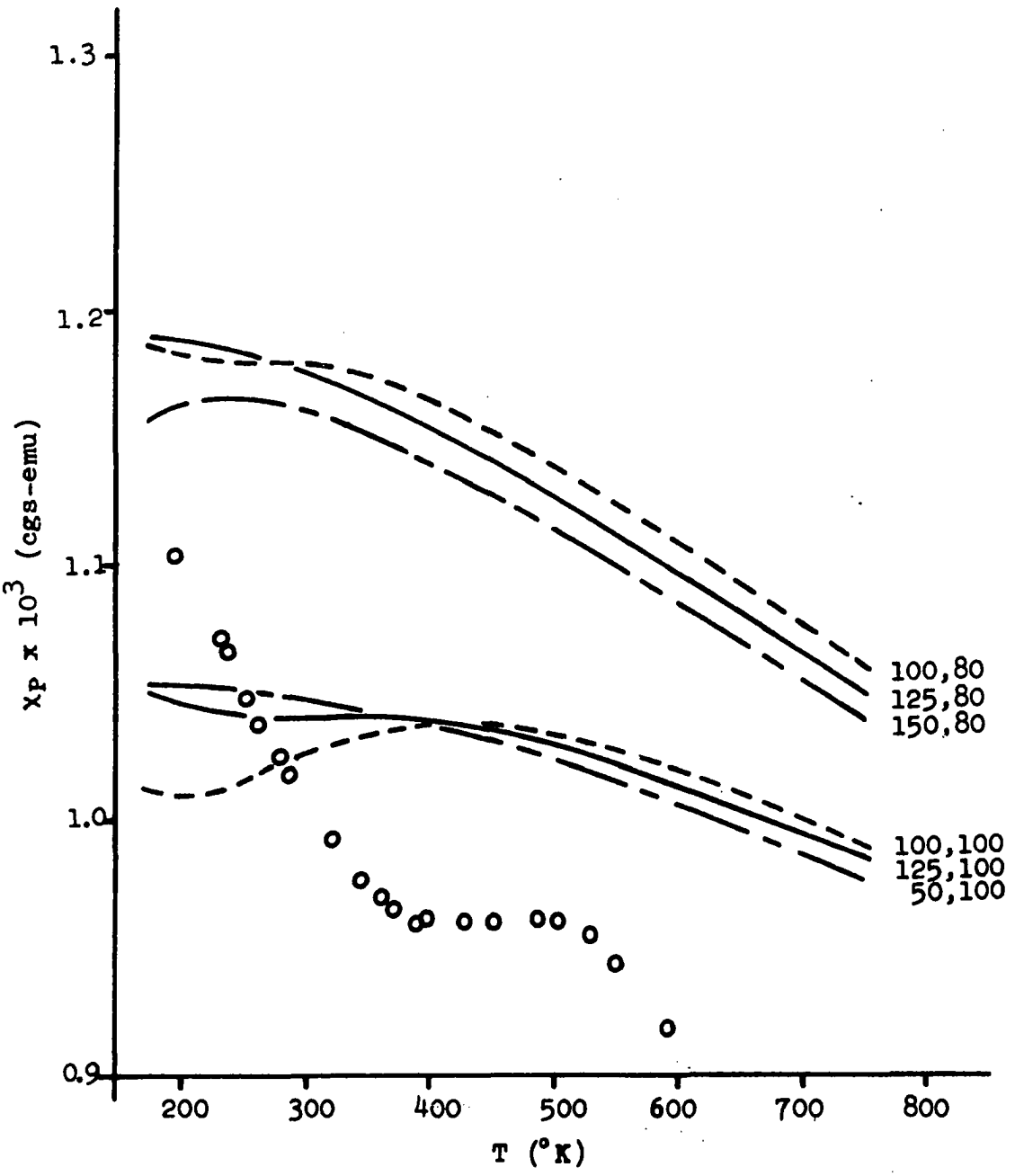


Figure 6. Orbital Contribution to Pair Susceptibility (per V^{3+} ion) for $\Delta_T = 1200$ cm^{-1}. Numbers to right of each curve are the J, J'z values in cm^{-1}. Circles are data from Ref. 37.

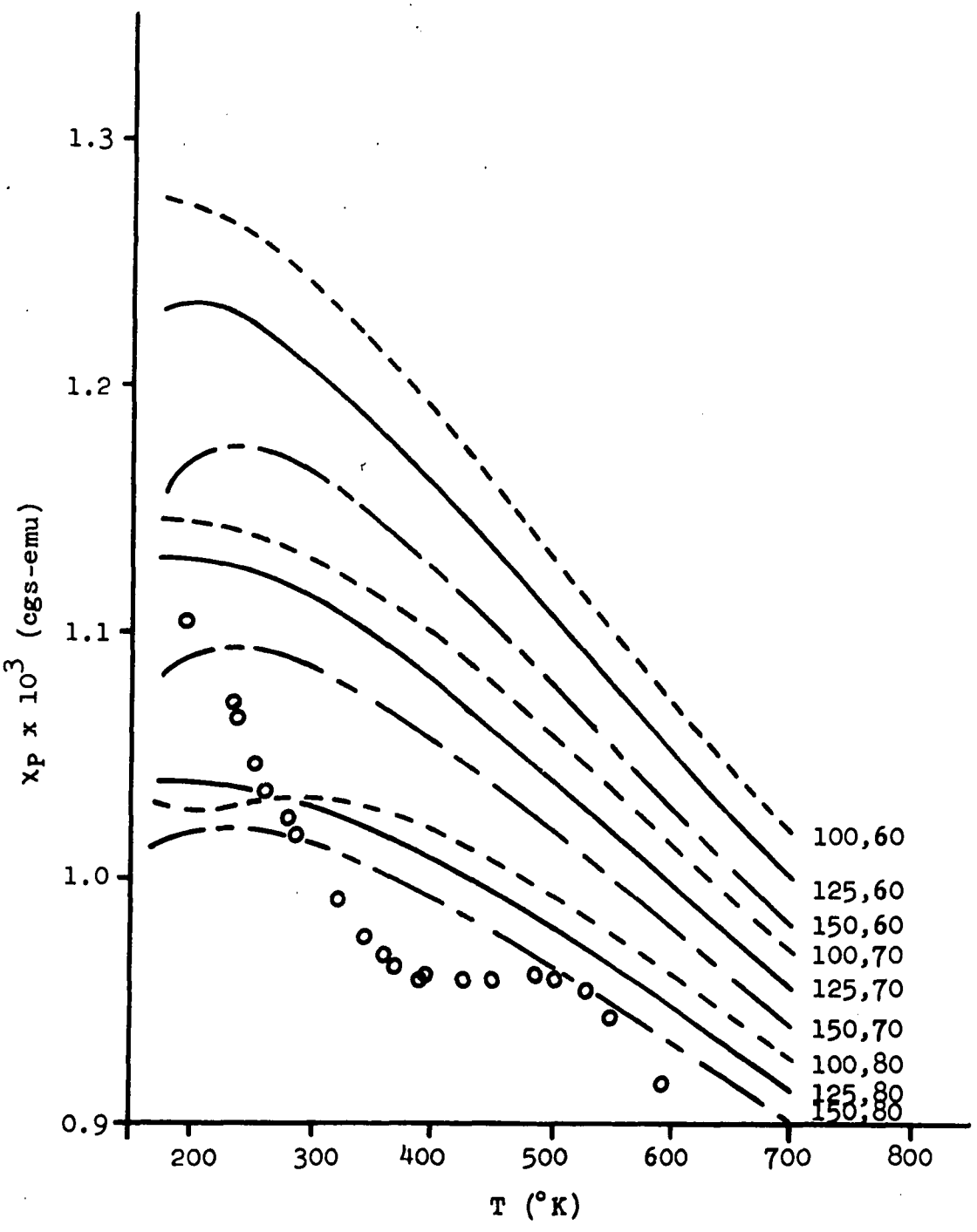


Figure 7. Orbital Contribution to Pair Susceptibility (per V^{3+} ion) for Δ_T = 2000 cm^{-1}. Numbers to right of each curve are J, J'z values in cm^{-1}. Circles are data from Ref. 37.

There are several features related to the transition which can be explained with the aid of an energy level diagram as in Fig. 8. The figure is drawn for the z-direction but the scheme is similar for the x-direction except the ±1 and ±2 magnetic levels are not split by the field. Since the magnetic field includes the molecular field the spacing of the M_S-levels depends on J'z. The important feature is the ordering of the M_S-levels for S = 1 and S = 2. The S = 1, M_S-levels are observed to be inverted relative to the S = 2, M_S-levels. This places the S = 1, M_S = 0 level and the S = 2, M_S = 0 level adjacent to each other on the vertical scale. Both of these are non-magnetic and as the temperature rises the lower one becomes populated first but only at the expense of the pair of magnetic levels just below it. However, since the magnetic spacing is small compared to J these three levels will be about equally populated when kT is comparable to J. This is even more true when J'z is small. But a further increase in temperature will elevate some of the pairs from the S = 1, M_S = 0 level to the S = 2, M_S = 0 with no change in the susceptibility. This is why the transition can be expected to occur over a range of temperatures as predicted by Goodenough (24). If the temperature is increased still further the thermal energy is sufficient to de-couple more pairs and the susceptibility begins to decrease as the graphs indicate.

The temperature for the onset of the transition

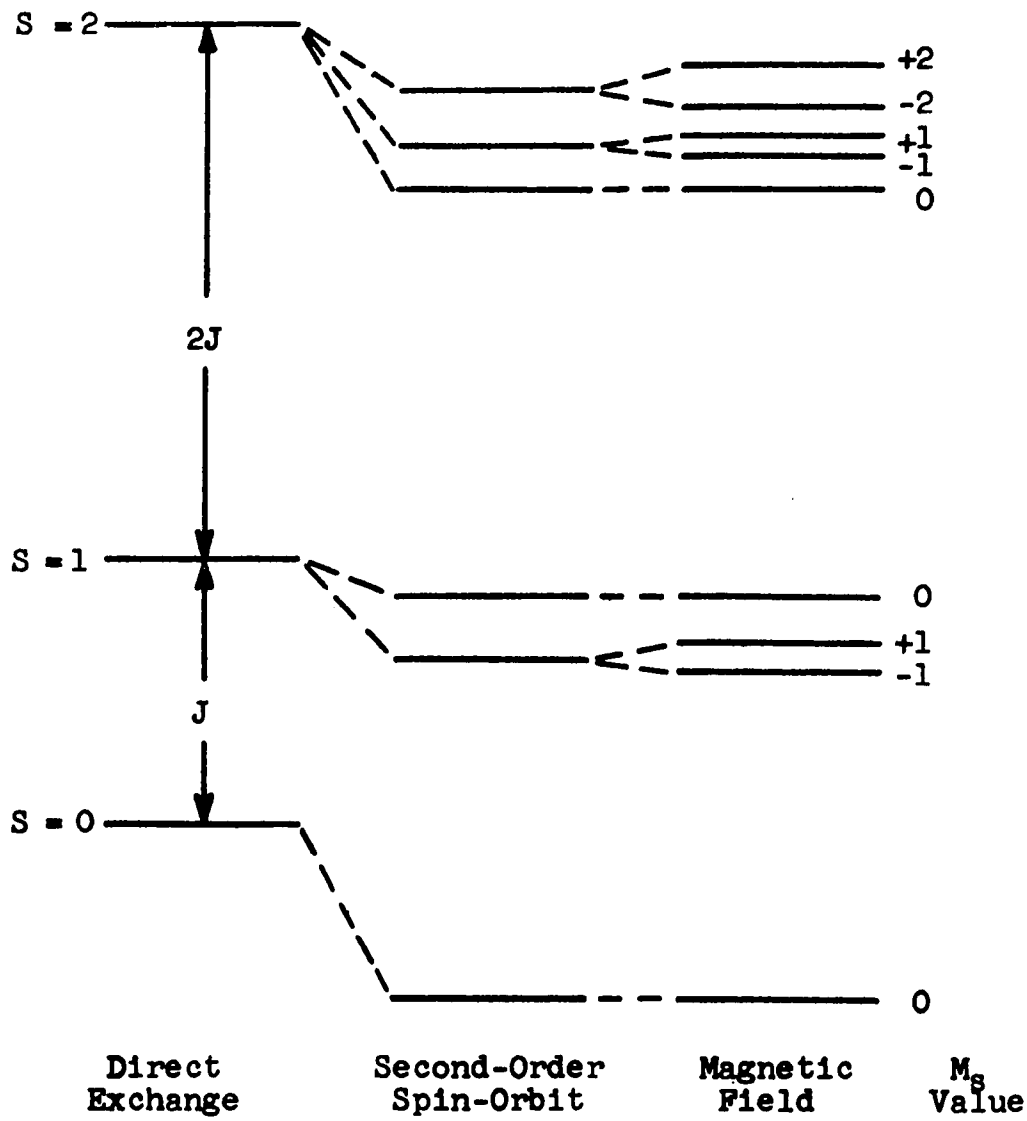


Figure 8. Schematic Energy Level Diagram for the Pair Orbital Ground State and for $\mathcal{H} = \mathcal{H}_Z$.

decreases with decreasing J since the S = 1 levels become populated more rapidly. The temperature range over which the transition may occur depends more strongly on J'z as shown in the graphs. Referring again to Fig. 8, the magnetic spacing of the S = 1, $M_S = \pm 1$ levels decreases with increasing J'z. This allows a greater energy separation between these levels and the S = 2, $M_S = 0$ level and T may increase considerably before the thermal energy begins to de-couple the spins. However, it is recognized that some interplay between J and J'z affects both the onset temperature and the range but the above considerations seem to have some merit, especially for a qualitative explanation.

One point which is almost incidental to this discussion is the fact that at low temperatures only the S = 0 level is populated. Thus, continued decrease in temperature should cause the susceptibility to decrease sharply. The temperature at which this occurs is the ordinary Neel point for antiferromagnets. This is a cooperative transition but is not very well-behaved in V_2O_3 because of the crystalline change at the transition temperature.

Application to Ti_2O_3

Ti_2O_3 also has the corundum structure but the magnetic ion only has a single 3d electron. Presumably, this is the reason the non-cooperative transition occurs in the low temperature phase of this crystal (24). Below about

250°K the magnetic susceptibility is extremely small indicating no appreciable magnetic moment. This is also confirmed by neutron diffraction data. If the exchange coupling is applied in this case to find the exchange levels for the pair one gets only two levels corresponding to S = 0,1 and separated in energy by the exchange parameter J. If the orbital effect is to account for the magnetic behavior in this crystal then the two $M_S = 0$ levels should be adjacent to each other on the vertical scale and, furthermore, they should both lie lower in energy than the two magnetic levels corresponding to $M_S = \pm 1$. However, to place the $M_S = 0$ level lower than the $M_S = \pm 1$ levels a zero-field splitting for the pair is required and an actual calculation of the energy levels did not produce such a splitting. This was not unexpected, though, since one is coupling two Kramer's doublets, neither of which is capable of being split in zero field. In fact, for S = 1 the levels are ordered according to $M_S = -1,0,1$ and the only way for the model to predict the magnetic behavior is for J to be extremely large for Ti_2O_3.

The above results are based on calculations for the z-direction only but experimental data shows practically no anisotropy throughout the range of temperature over which the transition occurs (24). Thus, it is doubtful that the model can explain the magnetic behavior of Ti_2O_3 because of the Kramer's degeneracy which is not present in V_2O_3.

CONCLUSION

The effect of Hylleraas-type correlation of the outer electrons has been studied for atoms having a $(2p)^2$ and $(3d)^2$ outer-electron configuration. This was done using, first, a screened coulomb potential for both types of atoms. The screening constant was determined for the $(2p)^2$ atoms by Slater's rules and by several other methods for the $(3d)^2$ atoms. In each case, the correlation function $(1 + cr_{12})$ was appended to the Clebsch-Gordan two-electron wave function and the correlation coefficient c was determined by the variation principle. It was found that c increased with the higher multiplet levels causing a differential suppression of these levels. This caused the multiplet spacings to be too close together to be considered an improvement.

The same procedure was repeated for the $(3d)^2$ atoms but the Hartree-Fock potential was used and the SCF radial functions were taken as the first-order functions for atoms where these were available and for those for which sufficient experimental data could be found. In this calculation, c still increased with energy but the resulting differential suppression was not as severe. While the levels were still drawn too close together there was satisfactory improvement

in the multiplet spacings. Suggestions are made for refining this calculation.

The magnetic properties of the $(3d)^2$ ion in V_2O_3 were also studied. Most of these appear when the ion is in the ^3F ground level and since the correlation coefficient for this level was very small, therefore affecting the energy of this level very little, it was not necessary to use the correlated wave function.

Several calculations were made in an effort to arrive at a model for the crystal which satisfactorily predicted the experimentally determined magnetic properties. A one-ion model was first used in which the electrostatic and magnetic environment of the central ion was treated phenomenologically as a perturbation to the free-ion energy levels. The electrical environment was represented by an electrostatic potential which satisfied Laplace's equation in the vicinity of the central ion. The magnetic environment was represented by an effective molecular field which had the direction of an externally applied magnetic field and a magnitude which was determined self-consistently. It was found that on the basis of this model the magnetic susceptibility data could be fitted in two different temperature regions but only with two different sets of adjustable parameters. One of these parameters, the trigonal field splitting, had to be considerably larger than the corresponding corundum value to obtain satisfactory agreement in both temperature

regions.

Because of the c-axis pairing of cations in the corundum structure it was possible to make another series of calculations in which the c-axis pairs were coupled together exactly by direct exchange interactions and the resulting homonuclear diatomic molecule was then coupled to the magnetic lattice by a self-consistent molecular field. This was done for the pure spin system, first, using an antiferromagnetic direct exchange and a ferromagnetic molecular field. The calculation was then repeated with these two fields interchanged. In neither case was it possible to predict the non-cooperative transition in V_2O_3 and only a qualitative agreement with experiment in the high temperature region could be claimed.

Finally, the coupled pair model was extended to include the orbital contribution. While quantitative agreement with experiment was not very good the results did predict the non-cooperative transition. It was possible to explain the formation of the transition on a physical basis using an energy level diagram. A brief discussion of what could be expected from the extended coupled pair model for Ti_2O_3 was also given and it appears that the model is not suitable for magnetic ions which exhibit Kramer's degeneracy.

APPENDIX I

MATRIX ELEMENT

In (2.15) the operator $r_{12}\ \vec{\nabla}_1\ r_{12} \cdot \vec{\nabla}_1$ appeared and it was indicated how this could be reduced to a constant. This derivation is given explicitly here. It is easy to show using Cartesian coordinates that

$$r_{12}\ \vec{\nabla}_1\ r_{12} = \frac{1}{2}\ \vec{\nabla}_1\ r_{12}^2$$

and

$$\vec{\nabla}_1\ r_{12}^2 = \vec{\nabla}_1\ (r_1^2 + r_2^2 - 2r_1 r_2 \cos\ \omega)$$

where ω is the angle between the two radius vectors $\vec{r}_1$ and $\vec{r}_2$. Now

$$\cos\ \omega = P_1(\cos\ \omega) = \frac{4\pi}{3} \sum_{m=-1}^{1} Y_1^m(1)\ Y_1^{m*}(2)\ ,$$

substituting,

$$\vec{\nabla}_1 r_{12}^2 = \vec{\nabla}_1 r_1^2 + r_2^2 \vec{\nabla}_1 - 2r_2 \cdot \frac{4\pi}{3} \sum_{m=-1}^{1} Y_1^{m*}(2)\ \vec{\nabla}_1 (r_1 Y_1^m(1))$$

and

$$\vec{\nabla}_1 r_{12}^2 \cdot \vec{\nabla}_1 = \vec{\nabla}_1 r_1^2 \cdot \vec{\nabla}_1 + \vec{\nabla}_1 r_2^2 \cdot \vec{\nabla}_1 -$$

$$2r_2 \cdot \frac{4\pi}{3} \sum_{m=-1}^{1} Y_1^{m*}(2)\ \vec{\nabla}_1 (r_1 Y_1^m(1)) \cdot \vec{\nabla}_1\ .$$

Now the diagonal element for two equivalent ℓ-electrons contains terms like

$$\tfrac{1}{2}(\varphi_\ell(1)\ \varphi_\ell(2)\,|\vec{\nabla}_1 r_{12}^2\cdot\vec{\nabla}_1\,|\varphi_\ell(1)\ \varphi_\ell(2))$$

$$= \tfrac{1}{2}(\varphi_\ell(2)\,|\varphi_\ell(2))(\varphi_\ell(1)\,|\vec{\nabla}_1 r_1^2\cdot\vec{\nabla}_1\,|\varphi_\ell(1))$$

$$+ 0 - \frac{4\pi}{3}\sum_{m=-1}^{1}(\varphi_\ell(2)\,|r_2 Y_1^{m*}(2)\,|\varphi_\ell(2))(\varphi_\ell(1)\,|\vec{\nabla}_1(r_1 Y_1^m(1))\,|\varphi_\ell(1)).$$

Consider each right-hand member separately. The first term simplifies as follows.

$$\tfrac{1}{2}(\varphi_\ell(2)\,|\varphi_\ell(2))(\varphi_\ell(1)\,|\vec{\nabla}_1 r_1^2\cdot\vec{\nabla}_1\,|\varphi_\ell(1)$$

$$= \tfrac{1}{2}\int R_{n\ell}(1)\,\frac{\partial r_1^2}{\partial r_1}\,\frac{\partial R_{n\ell}(1)}{\partial r_1}\,r_1^2 dr_1$$

$$= \int_0^\infty R_{n\ell}(1)\,r_1\,\frac{\partial R_{n\ell}(1)}{\partial r_1}\,r_1^2 dr_1 = -\frac{3}{2}\,.$$

The above integral has the same value no matter what $R_{n\ell}(1)$ is used as long as it is a well-behaved radial function. This is seen from integration by parts.

The second term is zero because

$$(\varphi_\ell(2)\,|r_2 Y_1^{m*}(2)\,|\varphi_\ell(2))$$

$$= \int_0^\infty |R_{n\ell}(2)|^2\,r_2^3 dr\cdot\int Y_\ell^{m'*}(2)Y_1^{m*}(2)Y_\ell^{m''}(2)\,d\Omega\,.$$

The angular integral is always zero since the sum of the three ℓ-values is $2\ell + 1$ which is always an odd integer. Thus, the result

$$\langle r_{12}\vec{\nabla}_1 r_{12}\cdot\vec{\nabla}_1\rangle = -3/2$$

which was to be proved.

APPENDIX II

(3d)-SCREENING FUNCTION

In the Hartree-Fock theory the function which represents the screening of one 3d-electron by the other was defined as

$$Y(r_1) = \frac{1}{r_1} \sum_k a^{(k)} Y_k(3d,3d;r_1) \ . \qquad \text{(II.1)}$$

In (II.1), $Y_k(3d,3d;r_1)$ is given by (4.8) where the radial functions are those of Watson, (4.11). The square of $R_{3d}(r)$ which appears in the integral can be written as

$$|R_{3d}(r)|^2 = \sum_{i=1}^{10} A_i \ r^4 \ e^{-b_i r} \qquad \text{(II.2)}$$

where the subscripted quantities are related to the C_i and s_i of (4.11) as follows.

$A_1 = C_{12}^2$ $\quad$ $A_8 = 2C_{13}C_{14}$ $\quad$ $b_5 = s_{12} + s_{13}$

$A_2 = C_{13}^2$ $\quad$ $A_9 = 2C_{13}C_{15}$ $\quad$ $b_6 = s_{12} + s_{14}$

$A_3 = C_{14}^2$ $\quad$ $A_{10} = 2C_{14}C_{15}$ $\quad$ $b_7 = s_{12} + s_{15}$

$A_4 = C_{15}^2$ $\quad$ $b_1 = 2s_{12}$ $\quad$ $b_8 = s_{13} + s_{14}$

$A_5 = 2C_{12}C_{13}$ $\quad$ $b_2 = 2s_{13}$ $\quad$ $b_9 = s_{13} + s_{15}$

$A_6 = 2C_{12}C_{14}$ $\quad$ $b_3 = 2s_{14}$ $\quad$ $b_{10} = s_{14} + s_{15}$

$A_7 = 2C_{12}C_{15}$ $\quad$ $b_4 = 2s_{15}$

When (II.2) is substituted into (4.8) and the integrations performed the results are:

$$Y_o(3d,3d;r_1) = 1 - 6! \sum_{i=1}^{10} \frac{A_i}{b_i^7} e^{-b_i r_1} \left(\frac{r_1^5}{b_i^2} + \frac{10}{b_i^3} r_1^4 + \frac{60}{b_i^4} r_1^3 + \frac{240}{b_i^5} r_1^2 + \frac{600}{b_i^6} r_1 + \frac{6!}{b_i^7} \right)$$

$$Y_2(3d,3d;r_1) = \sum_{i=1}^{10} A_i \left[\frac{8!}{b_i^9} \frac{1}{r_1^2} - e^{-b_i r_1} \left(\frac{5}{b_i^2} r_1^5 + \frac{50}{b_i^3} r_1^4 + \frac{330}{b_i^4} r_1^3 + \frac{1680}{b_i^5} r_1^2 + \frac{6720}{b_i^6} r_1 + \frac{20160}{b_i^7} + \frac{8!}{b_i^8} \frac{1}{r_1} + \frac{8!}{b_i^9} \frac{1}{r_1^2} \right) \right]$$

$$Y_4(3d,3d;r_1) = \sum_{i=1}^{10} A_i \left[\frac{10!}{b_i^{11}} \frac{1}{r_1^4} - e^{-b_i r_1} \left(\frac{9}{b_i^2} r_1^5 + \frac{90}{b_i^3} r_1^4 + \frac{720}{b_i^4} r_1^3 + \frac{5040}{b_i^5} r_1^2 + \frac{30240}{b_i^6} r_1 + \frac{151200}{b_i^7} + \frac{604800}{b_i^8} \frac{1}{r_1} + \frac{1814400}{b_i^9} \frac{1}{r_1^2} + \frac{10!}{b_i^{10}} \frac{1}{r_1^3} + \frac{10!}{b_i^{11}} \frac{1}{r_1^4} \right) \right]$$

Only three values of k appear because of the selection rules associated with 3d-wave functions.

BIBLIOGRAPHY FOR PART I

1. Breene, R. G., Jr., Phys. Rev. 128, 5 (1962).

2. Brickstock, A. and Pople, J. A., Phil. Mag., 43, 1090 (1952).

3. Cady, W. M., Phys. Rev., 43, 322 (1933).

4. Condon, E. U., and Shortley, G. H., The Theory of Atomic Spectra, Cambridge University Press (1959).

5. Freeman, A. J., and Watson, R. E., J. Phys. Soc. Japan, 17, SB-I,15 (1961).

6. Freeman, A. J., and Watson, R. E., Phys. Rev. 131, 2566 (1963).

7. Lane, N. F., and Lin, C. C., Ann. of Phys., 20, 2 (1962).

8. Lennard-Jones, Sir J. E., and Pople, J. A., Phil. Mag., 43, 581 (1952).

9. Moore, C. E., Atomic Energy Levels, Circular 467, U.S. Dept. of Commerce, National Bureau of Standards (1952).

10. Pauling, L., and Wilson, E. B., Introduction to Quantum Mechanics, McGraw-Hill Book Company, Inc., New York (1935).

11. Slater, J. C., Quantum Theory of Atomic Structure, Vol. 1, McGraw-Hill Book Company, Inc., New York (1960).

12. Slater, J. C., Quantum Theory of Atomic Structure, Vol. 2, McGraw-Hill Book Company, Inc., New York (1960).

13. Szasz, L. J. Chem. Phys., 35, 1072 (1961).

14. Szasz, L., Phys. Rev. 126, 169 (1962).

15. Watson, R. E., "MIT Solid State and Molecular Theory Group, Tech. Rept. 12", MIT, June 15, 1959.

16. Watson, R. E., and Freeman, A. J., Phys. Rev., 131, 26 (1963).

BIBLIOGRAPHY FOR PART II

17. Artman, J. O., and Murphy, J. C., J. Chem. Phys. 38, 1544 (1963).

18. Ballhausen, C. J., Ligand Field Theory, McGraw-Hill Book Company, Inc., New York, 1962.

19. Brumage, W. H., Quade, C. R., and Lin, C. C., Phys. Rev. 131, 949 (1963).

20. Carr, P. H., and Foner, S., J. Appl. Phys. Supp., 31, 344S (1960).

21. Foëx, M., and Wucher, J., Compt. rend. 241, 184 (1955).

22. Foner, S., Phys. Rev. 130, 183 (1963).

23. Goodenough, J. B., Phys. Rev. 117, 1442 (1960).

24. Goodenough, J. B., Magnetism and the Chemical Bond, Interscience Publishers, Inc., New York, 1963.

25. Hartman, H., and Schläfer, H. L., Z. Naturforsch. 6a, 754 (1951).

26. Kanamori, J., Prog. Theoret. Phys. 17, 177 (1957).

27. Kemble, E. C., The Fundamental Principles of Quantum Mechanics with Elementary Applications, Dover Publications, Inc., New York, 1958.

28. McClure, D. S., J. Chem. Phys. 36, 2757 (1962).

29. Morin, F. J., Phys. Rev. Letters, 3, 34 (1959).

30. Oguchi, T., Prog. Theoret. Phys. 13, 148 (1955).

31. Pratt, G. W., Jr., and Bailey, P. T., Phys. Rev. 131, 1923 (1963).

32. Quade, C. R., Master of Science Thesis, University of Oklahoma, 1960.

33. Selwood, P. W., Magnetochemistry, Interscience Publishers, Inc., New York, 1956, 2nd ed.

34. Van Vleck, J. H., J. Chem. Phys. 9, 85 (1941).

35. Van Vleck, J. H., The Theory of Electric and Magnetic Susceptibilities, University Press, London, 1932.

36. Warekois, E. P., J. Appl. Phys. Supp. 31, 346S (1960).

37. Wucher, J., J. Res. C.N.R.S., 4, 237 (1952).